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QUANTITATIVE
CHEMICAL ANALYSIS

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QUALITATIVE CHEMICAL ANALYSIS

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QUANTITATIVE CHEMICAL ANALYSIS

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PREFACE TO THE SECOND VOLUME.

THE second volume of this Edition of Fresenius' Quantitative Chemical Analysis is, from Part II. where the "Special Part" begins, not merely a new edition in the ordinary sense of the word, but rather an almost entirely new book, there being scarcely two consecutive pages which are identical with those of the previous edition.

The Special Part includes the analysis of potable waters, mineral waters, technical products, and minerals, as well as the estimation of sugars, alcohol, tanning materials, and anthracene; also the estimation of the inorganic matter in plants, the analysis of soils and manures, and the examination of atmospheric air. This part has been greatly extended and made far more comprehensive than in the preceding edition, consequent on the application of chemical analysis for the purposes of Hygiene, Commerce, Technical Industries, Metallurgy, and Agriculture, having become far more widely recognised than formerly.

The thorough revision of the "Special Part" afforded the late author of the book an opportunity of introducing the various analytical processes which had been published since the appearance of the former edition, such as Volhard's method of estimating silver, Bunsen's process for separating arsenic from antimony in the analysis of pyrites, and Kjeldahl's method for estimating organic nitrogen, including the various modifications of it which have been proposed; also new processes for the analysis of argol.

As the equivalents of many of the elements have been again determined since the appearance of Volume I. of the book, and the earlier determinations of the equivalent numbers have also been recalculated, the author has largely increased the tables given at the end of the volume so as to include the results of these

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investigations. In accordance, however, with the wishes of the late Dr. Fresenius, the notation and the atomic weights employed in the German Edition, have been retained in the English Translation which is, moreover, as literal as possible.

There is a full Table of Contents, and also a copious Index, which it is hoped will facilitate the use of the mass of valuable information contained in the book.

The Editor desires to thank Mr. C. Salter for the assistance he rendered in preparing the translation of this volume.

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DIVISION I.

THE EXECUTION OF ANALYSIS.

SECTION VI

ORGANIC ANALYSIS.

§ 171.

Organic compounds contain but comparatively few of the elements; a small number of them consist simply of 2 elements, viz.;

C and H;

the greater number contain 3 elements, viz., as a rule,

C, H, and O;

most of the rest 4 elements, viz., generally,

C, H, O, and N;

a small number 5 elements, viz.,

C, H, O, N, and S;

and a few, 6 elements, viz.,

C, H, O, N, S, and P.

This applies to all the natural organic compounds which have as yet come under our notice. But we may prepare organic compounds synthetically which contain other elements besides those enumerated; thus we know many organic substances, containing chlorine, iodine, or bromine; others, which contain arsenic, antimony, tin, zinc, platinum, iron, cobalt, &c.; and it is quite impossible to say what other elements may not in like manner be capable of becoming constituents of organic compounds.

With these compounds we must not confound those in which organic acids are combined with inorganic bases, or organic bases with inorganic acids, such as lead tartrate, borate of morphia, &c.; since in such bodies any of the elements may of course occur.

Organic compounds may be analysed either with a view simply to resolve them into their proximate constituents; thus, for instance, a gum-resin into resin, gum, and ethereal oil; or the analysis may have for its object the determination of the ultimate constituents (the elements) of the substance. The simple resolution of organic compounds into their proximate constituents is effected by methods perfectly similar to those used in the analysis of inorganic compounds; that is, the operator endeavours to separate (by solvents, application of heat, &c.) the individual constituents from one another, either directly, or after having converted them into appropriate compounds. We disregard here altogether this kind of organic analysis—of which the methods must be nearly as numerous and varied as the cases to which they are applied—and proceed at once to treat of the second kind, which may be called *the ultimate analysis of organic bodies.*

The ultimate analysis of organic bodies (*here termed simply, organic analysis*) has for its object, as stated above, the determination of the elements contained in organic substances. It teaches us how to isolate these elements or to convert them into compounds of known composition; to separate the new compounds formed from one another; and to calculate from their several weights, or volumes, the quantities of the elements. Organic analysis, therefore, is based on the same principle as most of the methods employed for separating and determining inorganic compounds.

As the conversion of most organic substances into distinctly characterized and readily separable products, the weights of which can be accurately determined, offers no great difficulties, organic analysis is usually one of the more easy problems of analytical chemistry;—and as, from the limited number of the elements which constitute organic bodies, there is necessarily a great sameness in the products of their decomposition, the analytical process is always very similar, and a few methods suffice for all cases. It is principally owing to this latter circumstance that organic analysis has so speedily attained its present high degree of perfection:—the constant examination and improvement of a few methods by a great number of chemists could not fail to produce this result.

An organic analysis may have for its object either simply to ascertain the relative quantities of the constituent elements of a substance—thus, for instance, woods may be analysed to ascertain their heating power, fats to ascertain their illuminating power—or to determine not only the relative quantities of the constituent elementary atoms, but also their absolute quantities, that is, to determine the number of equivalents of carbon, hydrogen, oxygen, &c., which constitute 1 equivalent of the analysed compound. In scientific investigations, the latter object is the one invariably sought, although we are not yet able to attain it in all cases. These two objects cannot well be attained by one operation; each requires a distinct process.

The methods by which we ascertain the proportions of the constituent elements of organic compounds may be called, collectively, *the ultimate analysis of organic bodies*, in a more restricted sense; whilst the methods which reveal to us the absolute number of elementary equivalents constituting the complex equivalent of the analysed compound may be styled *the determination of the equivalents of organic bodies.*

The success of an organic analysis depends both on the method and its execution. The latter requires patience, circumspection, and skill; whoever is moderately endowed with these gifts will soon become a proficient in this branch. The selection of the method depends on our knowledge of the constituents of the substance, and the method selected may require certain modifications, according to the properties and state of aggregation of the same. Before we can proceed, therefore, to describe the various methods applicable in the different cases that may occur, we have first to consider the means of testing organic bodies qualitatively.

I. QUALITATIVE EXAMINATION OF ORGANIC BODIES.

§ 172.

It is not necessary, for the correct selection of the proper method, to know all the elements of an organic compound, since, for instance, the presence or absence of oxygen makes not the slightest difference to the method. But with regard to other elements, such as nitrogen, sulphur, phosphorus, chlorine, iodine, bromine, &c., and also the various metals, it is absolutely indispensable that the operator should know positively whether one or other of them is present. This may be ascertained in the following manner :—

1. *Testing for Nitrogen.*

When substances containing a tolerably large amount of nitrogen are burned, or strongly heated, they give off the well-known smell of singed hair or feathers. If this smell is distinctly perceptible, no further test is required, but if not, the substance should be examined by one of the following methods :—

a. The substance is mixed with hydrate of potassa in powder, or with soda-lime (§ 66, 4), and the mixture heated in a test-tube. If the substance contains nitrogen, ammonia will be evolved, which may be readily detected by its odor and reactions, and by the formation of white fumes with volatile acids. Should these reactions fail to afford positive certainty, every doubt may be removed by the following experiment :—Heat a somewhat larger portion of the substance, in a short tube, with an excess of soda-lime, and conduct the products of the combustion into dilute hydrochloric acid; evaporate the acid on the water-bath, dissolve the residue in a little water, mix the solution with bichloride of platinum, evaporate nearly to dryness on a water-bath, and treat the residue with alcohol. If the residue dissolves without leaving any double chloride of platinum and ammonium, the substance may be considered to be free from nitrogen.

b. LASSAIGNE has proposed another method, which is based on the property of potassium or sodium to form a cyanide when ignited with a nitrogenous organic substance. The following is the best mode of performing the experiment :—

Heat the substance under examination, in a test-tube, with a small piece of potassium or sodium, and, after the complete combustion of the metal, treat the residue with a little water (cautiously); filter the solution, add two drops of solution of sulphate of protoxide of iron containing some sesquioxide, digest the mixture a short time, and add hydrochloric acid in excess. The formation of a blue or bluish-green precipitate or coloration proves the presence of nitrogen.

Both methods are delicate : *a* is the more commonly employed, and suffices in almost all cases; *b* does not answer so well in the case of alkaloids containing oxygen (*e.g.*, morphine, brucine).

c. In organic substances containing oxides of nitrogen, the presence of nitrogen cannot be detected with certainty by either *a* or *b*, but it may be readily discovered by heating the substance in a tube, when red acid fumes, imparting a blue tint to iodide of potassium and starch paper, will be evolved, often accompanied by deflagration.

2. *Testing for Sulphur.*

a. Solid substances are fused with about 12 parts of pure hydrate of potassa and 6 of nitrate of potassa; or they are intimately mixed with some pure nitrate of potassa and carbonate of soda, and the mixture is gradually added to nitrate of potassa heated to fusion in a porcelain crucible. The mass is allowed to cool, then dissolved in water, and the solution, after being acidified with hydrochloric acid, is tested with chloride of barium. Particular care must be taken that the reagents are free from sulphuric acid, and in exact experiments the fusion must be conducted over a spirit-lamp, otherwise an error may arise from the sulphur present in coal-gas.

b. Liquids are treated with fuming nitric acid, or with a mixture of nitric acid and chlorate of potassa, at first in the cold, finally with application of heat; the solution is evaporated nearly to dryness, diluted, filtered if necessary, and tested as in *a.*

c. If a small quantity of a dry organic substance containing sulphur is heated with a very small piece of sodium, in a tube sealed at one end, the sulphur is converted into sulphide of sodium, which passes into solution on treating the fragments of the lower part of the tube with water, and may be detected by one of the methods given in *d* (VOHL,* SCHÖNN†).

d. As the methods *a*, *b*, and *c* serve simply to indicate the presence of sulphur in a general way, but afford no information regarding the state or form in which that element may be present, another method is here given, which serves to detect sulphur in organic compounds in the unoxidized state only.

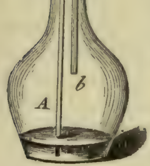

Fig. 1.

The substance is boiled with a strong solution of potassa, and evaporated nearly to dryness. The residue is dissolved in a little water, poured into the small flask *A* (fig. 1), and dilute sulphuric acid slowly added through the funnel-tube *c*; if sulphur is present, the slip of paper *b*, which has been moistened with a solution of acetate of lead, and then touched with a few drops of solution of carbonate of ammonia, will turn brown. It need hardly be mentioned that the cork must not fit air-tight.

The sulphide of potassium formed may also be detected by means of a solution of oxide of lead in soda, or of a polished surface of silver, or by nitroprusside of sodium (see "Qual. Anal." § 156).

3. *Testing for Phosphorus.*

a. The methods described in 2, *a* and *b*, may likewise be employed for phosphorus. The solutions obtained are tested for phosphoric acid with sulphate of magnesia, chloride of ammonium, and ammonia; or with sesquichloride of iron, with addition of acetate of soda; or preferably with a nitric acid solution of molybdate of ammonia (comp. "Qual. Anal." § 142). If method *b* is employed, the greater part of the excess of nitric acid must first be removed by evaporation.

b. In many cases the following method of SCHÖNN'S‡ may be employed with advantage. The organic substance is carbonized in a covered crucible, the mass pulverized and mixed with half its volume of magnesium powder; it is then put into the lower part of a thin glass tube sealed at one end, and heated rather strongly, shaking the tube at the same time so that the charred mass may not be driven out. If the substance contains phosphorus, a phosphorescence will be noticed in the dusk in the upper part of the tube, and occasionally some yellow or red phosphorus may be seen on the sides. The remainder of the phosphorus is in the residue in form of phosphide of magnesium. If the lower part of the tube is broken off, moistened with water, and gently warmed, the well-known odor of phosphoretted hydrogen will be perceived.

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* Zeitschr. f. anal. Chem. 2, 442. † *Ib.* 8, 52. ‡ *Ib.* 8, 55.

4. *Testing for Iodine, Bromine, and Chlorine.*

As regards the testing of organic substances for iodine, bromine, and chlorine I refer to § 190. I will here only give two methods which will suffice in most cases.

a. The dry organic substance is sprinkled on the bottom of a test-tube heated to redness. Iodine may often be detected by the colour of its vapour. On turning the contents of the tube into a wider one containing water and a little ammonia, hydriodic, hydrobromic, or hydrochloric acid may after a short time be detected in the liquid by the usual methods (see "Qual. Anal."). If the organic substance is a liquid, fill a small bulb-tube with it (§ 180), place the latter, with its tube open and downwards in a test-tube, ignite the bottom of the test-tube, and then cause some of the fluid to flow out by warming the bulb (ERLENMEYER*).

b. In BEILSTEIN's method † some powdered oxide of copper is ignited in the loop of a platinum wire, moistened with water, and again ignited; there should be no coloration of the flame, or the oxide of copper cannot be used for this purpose. Now take up some of the substance on the oxide of copper, and hold in a Bunsen flame near the lower and inner edge. The carbon burns first, and immediately afterwards a characteristic blue or green color is seen, if chlorine, bromine, or iodine is present (see "Qual. Anal.").

5. *Testing for Inorganic Substances.*

A portion of the substance is heated on platinum foil, to see if it leaves any residue. With difficultly combustible substances, the process may be accelerated by heating the spot on the platinum foil where the substance is to the most intense redness by directing the flame of the blowpipe upon it from below. Occasionally complete combustion is best effected by adding oxide of mercury to the residue left on ignition, and igniting again. The residue is then examined by the usual methods. It need hardly be mentioned that volatile metals in volatile organic compounds—*e.g.*, arsenic in kakodyl—cannot be detected by this method.

These preliminary experiments should never be omitted, since neglect in this respect may give rise to very serious errors. Thus, for instance, taurine, a substance in which a large proportion of sulphur was afterwards found to exist, had originally the formula $C_4NH_7O_{10}$ assigned to it.

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* Zeitschr. f. anal. Chem. 4, 137.

† *Ib.* 12, 95.

II. DETERMINATION OF THE ELEMENTS IN ORGANIC BODIES.

§ 173.

It is not my intention to give an account of the rise and progress of organic analysis; I shall therefore confine myself to the description of the most simple, precise, and universally applicable methods, omitting all the others. The more simple methods, which generally form part of the ordinary course of the student, will be fully described; whilst the more complicated methods, which presuppose a more advanced knowledge of the general manipulations of organic analysis, will be given more briefly. In the choice of methods, it must be remembered that, whilst those dependent on the use of complicated apparatus may be suited to laboratories where these analyses are of every-day occurrence, those methods in which more simple apparatus are used are better adapted to laboratories where these analyses are only undertaken occasionally.

As the accuracy of the results depends as much on the appropriate construction and arrangement of the apparatus as on the execution itself, I am anxious to impress upon the student that equal care must be bestowed upon both. I may add that he cannot with impunity deviate from the rules laid down, as they are the fruit of the long experience and the innumerable experiments of the most distinguished chemists.

In order to give a clear notion of the somewhat extensive subject treated in the following pages, a table is appended showing the order in which the different methods are treated.

A. SUBSTANCES CONSISTING OF CARBON AND HYDROGEN, OR OF CARBON, HYDROGEN, AND OXYGEN.

- *a.* *Solid bodies.*
  - α. Readily combustible, non-volatile bodies. Combustion with oxide of copper.
    1. LIEBIG'S process, § 174.
    2. BUNSEN'S modification, § 175.
  - β. Difficultly combustible, non-volatile bodies.
    1. Combustion with chromate of lead (and bichromate of potash), § 176.
    2. Combustion with oxide of copper and chlorate or perchlorate of potash, § 177.
    3. Combustion with oxide of copper and oxygen gas, § 178.
  - γ. Volatile bodies, or bodies undergoing alteration at 100°, § 179.
- *b.* *Liquid bodies.*
  - α. Volatile bodies, § 180.
  - β. Non-volatile bodies, § 181.

Supplement to *A*, § 182.
Modified apparatus.

B. SUBSTANCES CONSISTING OF CARBON, HYDROGEN, OXYGEN, AND NITROGEN.

- *a.* *Estimation of carbon and hydrogen*, § 183.

b *Estimation of nitrogen.*

- *a* From the volume.
  - 1. Relative method, § 184.
    - *aa.* After Liebig.
    - *bb.* After Bunsen.
    - *cc.* After Marchand and Gottlieb.
  - 2. Absolute estimation of nitrogen, § 185.
    - *aa.* After Dumas.
    - *bb.* After Simpson.
- *β.* Estimation of nitrogen by conversion into ammonia, after Varrentrapp and Will, § 186.
- *γ.* Modification of Varrentrapp and Will's method, by Péligot, § 187.

C. Analysis of Bodies containing Sulphur, § 188.

D. Estimation of Phosphorus in Organic Bodies, § 189.

E. Analysis of Substances containing Chlorine, Bromine, or Iodine, § 190.

F. Analysis of Organic Substances containing Inorganic Bodies, § 191.

Supplement to §§ 174—191.

Direct estimation of oxygen, and methods differing from the usual methods, § 192.

A. Analysis of Compounds which consist simply of Carbon and Hydrogen, or of Carbon, Hydrogen, and Oxygen.

The principle of the method which serves to effect the quantitative analysis of such compounds, and which was first proposed in its present form by Liebig, is exceedingly simple. The substance is burned to carbonic acid and water; these products are separated from each other and weighed, and the carbon of the substance is calculated from the weight of the carbonic acid, the hydrogen from that of the water. If the sum of the carbon and hydrogen is equal to the original weight of the substance, the substance contains no oxygen; if it is less than the weight of the substance, the difference expresses the amount of oxygen present.*

The combustion is effected either by igniting the organic substance with oxygenized bodies which readily part with their oxygen (oxide of copper, chromate of lead, &c.); or at the expense both of free and combined oxygen.

a. SOLID BODIES.

a. Readily combustible, non-volatile substances (*e.g.*, sugar, starch, tartaric acid).†

Combustion with Oxide of Copper.

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* The methods that have been proposed for the direct determination of oxygen in organic bodies have as yet had no important influence on organic analysis. They will be described in § 192.

† It need hardly be mentioned that readily combustible substances may be treated by the methods given below for difficultly combustible substances, and indeed recently these methods, which afford greater security as regards the combustion of the carbon, are generally preferred to the older methods, which are distinguished by their simplicity.

1. LIEBIG'S METHOD.

§ 174.

I. Apparatus and Preparations required for the Analysis.

To facilitate the matter for beginners, all the things with which they must provide themselves before an analysis can be commenced are here enumerated.

1. THE SUBSTANCE.—This must be most finely pulverized and perfectly pure and dry;—for the method of drying, see § 26. Substances which may undergo change on drying in air must be heated in a current of dry carbonic acid or hydrogen (ROCHLEDER*).

Fig. 2.

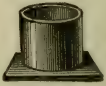
Fig. 3.

2. A TUBE IN WHICH TO WEIGH THE SUBSTANCE (fig. 2).—A small, perfectly dry glass tube, 4 or 5 cm. long, and about 1 cm. wide. It is closed with a light glass stopper, ground in, or with a cork covered with tinfoil. Its weight, including the stopper, must be known to a centigramme. It is advisable to place the tube in the drying apparatus, together with the substance intended for analysis. On the balance, the tube is either laid down or placed in a little foot made of tin (see fig. 3).

3. THE COMBUSTION TUBE.—A long tube of difficultly fusible glass (potash glass) is chosen, with a bore of 12 or 14 mm., and about 2 mm. thick in the glass. It is cleaned with linen or paper with the aid of a wire or string, and a length of 90 cm. cut off neatly. This piece is uniformly softened in the middle before a glass-blower's lamp, by constantly turning it round, and taking care not to confine the heat too much to one spot; the tube is then drawn out as represented in fig. 4, and finally apart at *b*. The fine points of the two pieces are sealed and thickened a little in the flame, and the sharp edges of the open ends, *a* and *c*, are slightly rounded by fusion, care being taken to leave the aperture perfectly round. The hinder part of the tube should be shaped as shown in fig. 5, and not as in fig. 6. Two perfect combustion tubes are thus produced. The one intended for immediate use is then thoroughly dried. This is effected either by laying

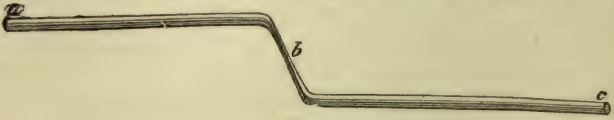

Fig. 4.

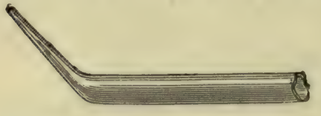
Fig. 5.

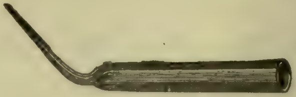
Fig. 6.

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* Zeitschr. f. anal. Chem. 6, 235.

the tube, with a piece of paper twisted over its mouth, for some time on a hot-plate or sand-bath, with occasional removal of the air from it by suction with the aid of a glass tube, or more rapidly by moving the tube to and fro over the flame of a gas- or spirit-lamp, heating its entire length, and continually removing the hot air by suction through the small glass tube (fig. 7). The suction is most conveniently effected by the water-pump; failing that, the mouth may be used. The combustion tube, when quite dry, is closed air-tight with a dry cork, and kept in a warm place until required for use.

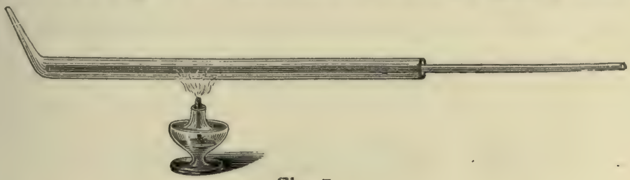

Fig. 7.

In default of glass tubes possessed of the proper degree of infusibility, brass or copper foil, or brass gauze, is rolled round the tube, and fastened with iron wire.

4. The Potash Bulbs (fig. 8).—This apparatus was devised by **Liebig.** It is filled, to the extent indicated in the engraving, with a clear solution of caustic potash of 1·27 sp. gr., which should be as free as possible from carbonate of potassa (§ 66, 6, vol. I.).* The introduction of the potash solution into the apparatus is effected by plunging the end *a* (but on no account the other end) into a beaker or dish into which a little of the solution has been poured out, and applying suction to *b*, either by means of a caoutchouc tube, or (and this is the safest way) with the aid of a small suction tube (fig. 9). The two ends are then wiped perfectly dry with twisted slips of paper, and the outside of the apparatus with a clean cloth.†

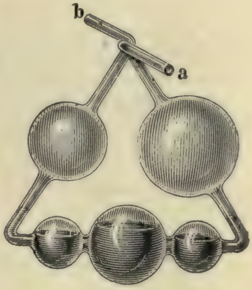

Fig. 8.

5. The Chloride of Calcium Tube.—Fig. 10 shows it in its simplest and original form. It is filled in the following manner:—In the first place, the aperture *a* of the tube *b a* is loosely stopped with a small cotton-wool plug, reaching about 1 cm. into the tube; this is effected by introducing a very loose cotton-wool plug into *c*, and applying a sudden and energetic suction at *b*. The bulb of the tube is then filled

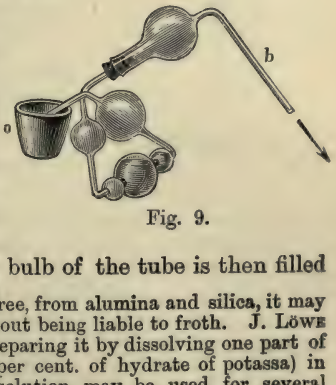

Fig. 9.

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* If the potash is pure, *i.e.*, free, or nearly free, from alumina and silica, it may be used in a much more concentrated state without being liable to froth. J. Löwe (Zeitschr. f. anal. Chem. 9, 220) recommends preparing it by dissolving one part of good caustic potash (which contains about 80 per cent. of hydrate of potassa) in one part of water. Bulbs filled with this solution may be used for several combustions without refilling.

† For other apparatus which may be used as substitutes for Liebig's bulbs see § 182

with lumps of chloride of calcium (§ 66, 7, *a*, vol. I.), and the tube *c d* up to *e* with smaller fragments, intermixed with coarse powder of the same substance; a loose cotton-wool plug is then inserted, and the tube finally closed with a perforated cork, into which a small glass tube is fitted; the protruding part of the cork is cut off, and the cut surface covered over with sealing-wax; the edge of the little tube *f g* (fig. 11) is slightly rounded at *g* by fusion.

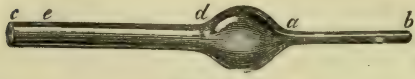

Fig. 10.

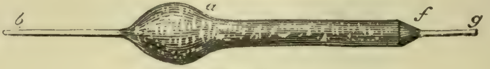

Fig. 11.

The tube illustrated by fig. 12 is more convenient, as a considerable quantity of the water condenses in the empty bulb *a*, and at the close of the experiment may be poured out. The operator is thus enabled to test it as to reaction, &c., and also to use the same tube far oftener without fresh filling than he could in the case of a tube unprovided with an empty bulb. Another form which is more convenient to weigh, is MARCHAND'S (fig. 13). In this also, the bulb *a* next to the combustion tube remains empty. In order to avoid the perforated cork, VOLHARD* recommends the form shown in fig. 14. Lastly, these two forms may be combined as shown in fig. 15 (H. FRESENIUS †).

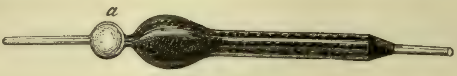

Fig. 12.

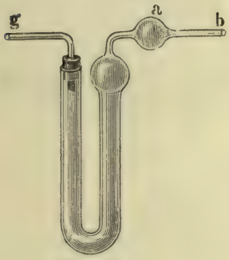

Fig. 13.

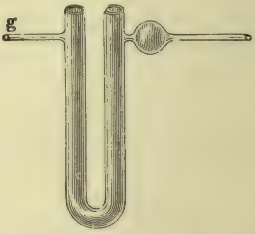

Fig. 14.

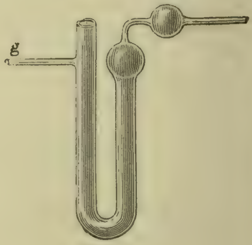

Fig. 15.

In order to be quite sure that the chloride of calcium tube only absorbs water and not small quantities of carbonic acid as well (for the salt usually has a slightly alkaline reaction), a slow current of dry carbonic acid should be passed through the prepared tube, and afterwards dry air, until the carbonic acid is again entirely displaced.

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* Ann. d. Chem. 176, 339; Zeitschr. f. anal. Chem. 14, 333.

† Zeitschr. f. anal. Chem. 14, 334.

6. A Small Tube of Vulcanized India-rubber —This must be so narrow that it can only be pushed with difficulty over the tube *g* of the chloride of calcium tube on the one hand, and over the end *a* of the potash bulbs on the other; in this case there is no need of binding with silk cord. If the vulcanized india-rubber tube should be a little too wide, it must be tied round with silk cord, or with copper wire. It is self-evident that the tube *g* of the chloride of calcium tube should be of the same width as the tube *a* of the potash bulbs. The india-rubber tube is purified from any adherent sulphur, and dried in the water-bath previous to use.

7. Corks.—These should be soft and smooth, and as free as possible from visible pores. A cork should be selected which fits perfectly tight, and screws with some difficulty to one-third of its length, at the most, into the mouth of the combustion tube; a smooth round hole, into which the end *b a* of the chloride of calcium tube must fit perfectly air-tight, is carefully bored through the axis of the cork by means of a fine round file. The cork is then kept for a long time in the water-bath. It is advisable always to have two corks of this description ready. Instead of ordinary corks, caoutchouc stoppers may be used, as recommended by Sonnenschein,* who describes them as durable, tight-fitting, and non-hygroscopic.† They are now frequently used instead of corks.

8. A Mixing Mortar.—A porcelain mortar, of greater width than depth, with a lip, and free from indentations and cracks; it should not be glazed inside. Previous to use, it is washed, allowed to dry in a warm place, and left there until required.

9. A Suction Tube.—Fig. 16 illustrates the most appropriate form. The aperture *a* is closed with a perforated cork, into which the tube *b* of the potash apparatus is fitted. A caoutchouc tube may be advantageously used instead of a perforated cork.‡

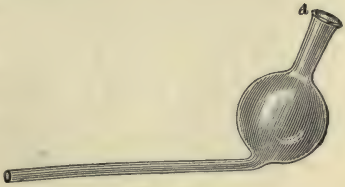

Fig. 16.

10. A Glass Tube, open at both ends, about 60 cm. long, and of sufficient width to admit being pushed over the tail of the combustion tube, where it is supported by means of a filtering stand.§

11. A sheet of glazed paper, with cut edges.

12. Oxide of Copper.—A Hessian crucible, of about 100 c. c. capacity, is nearly filled with oxide of copper prepared as directed in § 66, 1 (vol. I.); || the crucible is covered with a well-fitting overlapping lid, and

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* Journ. f. prakt. Chem. 67, 153.

† Compare, however, Dibbits, Zeitschr. f. anal. Chem. 15, 157.

‡ Until lately the mouth was almost invariably used for suction, but now an aspirator is generally used.

§ This tube is now usually replaced by a system of tubes containing soda-lime and chloride of calcium.

|| If the copper scales employed in making the oxide contain lime, they should be digested first with water containing a little nitric acid for some time, washed, and then, either immediately or after ignition in a muffle, treated with nitric acid free from chlorine. Oxide of copper containing chloride is best purified, according to E. Erlenmeyer, by igniting it in a tube, first in a current of moist air, and then, when the escaping fumes cease to redden litmus paper, in a current of dry

heated to dull redness with charcoal, or in a suitable gas furnace;* it is then allowed to cool, so that, by the time the oxide of copper is required for use, it can only just bear to be touched by the hand.

13. An Air-pump with Chloride of Calcium Tube.—See fig. 24. For the manner of performing an organic analysis without the aid of this apparatus, compare §§ 176, 178, 179.

14. Hot Sand.—The temperature of this should exceed 100°, but must not be sufficiently high to singe paper. It is either taken from the sand-bath, or must be specially heated for the purpose.

15. A Wooden Trough for the sand, see fig. 24.

16. A Combustion Furnace.—Some time ago the only one used was Liebig's, in which charcoal is the fuel. Subsequently spirit furnaces came into use, and at the present time gas combustion furnaces have been introduced into most laboratories; not that they are actually better, but because they are more cleanly and convenient. We shall consider first the charcoal furnace and then the gas furnaces.

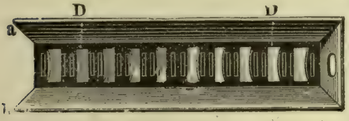

Fig. 17.

a. Liebig's combustion furnace is of sheet iron, in the form of a long box, open at the top and at one end. It serves to heat the combustion tube by means of red-hot charcoal. Fig. 17 represents the furnace as seen from the top. It is from 50 to 60 cm. long, and from 7 to 8 deep; the bottom, which, by cutting small slits in the sheet iron, is converted into a grating, has a width of about 7 cm. The side walls are inclined slightly outward, so that they are about 12 cm. apart at the top. A series of upright pieces of strong sheet iron, having the form shown in D, fig. 18, and rivetted on the bottom of the furnace at intervals of about 5 cm., serves to support the combustion tube. They must be of a height exactly corresponding with the round aperture in the front piece of the furnace (fig. 18, A). This aperture must be sufficiently large to admit the combustion tube easily.

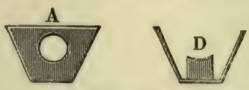

Fig. 18.

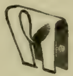

Fig. 19.

Of the two screens, the one has the form shown in fig. 19, the other that shown in fig. 18, A, with the border turned down at the upper edge. The openings cut into the screens must be sufficiently large to receive the combustion tube without difficulty. The furnace is placed upon two bricks resting upon a flat surface, and is slightly raised at the farther end, by inserting a piece of wood under the supports (see fig. 26). The apertures of the grating at the anterior end of the furnace must not be blocked up by the supporting bricks. In cases where the combustion tubes are of a good quality, the back end of the furnace

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air; by these operations all remains of oxides of nitrogen are also removed. Oxide of copper may be prepared so as to be with certainty free from all injurious impurities by dissolving the galvanically precipitated metal in pure nitric acid, evaporating and igniting (C. Reischauer, Zeitschr. f. anal. Chem. 2, 197; J. Löwe, *Ib.* 9, 217).

* Zeitschr. f. anal. Chem. 2, 194.

may be raised more advantageously by introducing a little iron rod or a piece of a tile between the furnace and the supporting brick; this arrangement will give the air free access to all the holes of the grating; or the furnace may also be directly placed upon a tripod—which, in fact, is now the usual way. Placing the tube in a gutter of very thin sheet iron tends greatly to preserve it. A charcoal furnace with regulated access of air has been recommended by Gawalovski.*

b. Gas combustion furnaces of widely different kinds have been proposed.† Fig. 20 represents one which is very frequently employed.‡

The apparatus consists of two parts, the system of burners and the support. The system of burners consists of from 15 to 25 Bunsen burners, each of which is provided with a separate stop-cock and a ring to regulate the access of air. The burners are screwed into a tube from 48 to 78 cm. long, and 25 mm. wide, which is connected with the gas supply. The tubes of the burners are flattened at the top. The iron stand shown in fig. 20 is v. Babo's, with Erlenmeyer's improvement.§ The flames enter through a slit-shaped opening, and play round the combustion tube, escaping above through an opening also in the form of a slit. The combustion tube lies on magnesia or asbestos in an iron-plate trough, or on a trough of fire-clay provided, according to

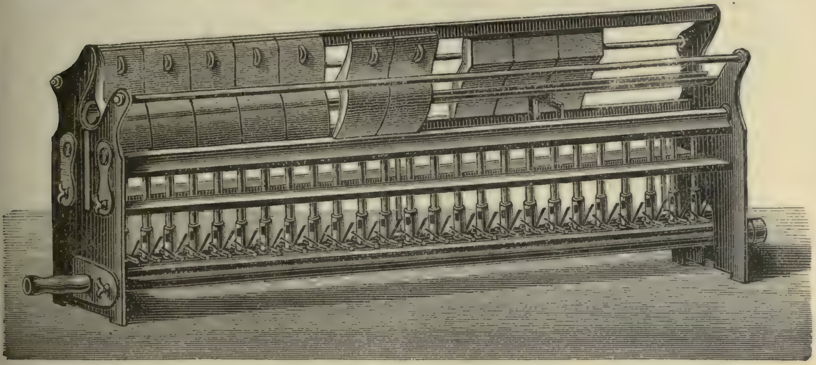

Fig. 20.

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* Zeitschr. f. anal. Chem. 14, 309.

† Compare the papers of v. Baumhauer (Annal. d. Chem. u. Pharm. 90, 21), A. W. Hofmann (Q. J. C. S. 6, 209), Sonnenschein (Journ. f. prakt. Chem. 55, 478), Magnus (*Ib.* 60, 32), Wetherill (Liebig-Kopp's Jahresb. 1855, 828), Pebal (Annal. d. Chem. u. Pharm. 95, 24), J. Lehmann (*Ib.* 102, 180), v. Babo (Ber. über die Verhandl. der Gesellsch. f. Beförderung der Naturw. zu Freiburg im Br. 1857, Nr. 22 u. 23), Heintz (Pogg. Annal. 103, 142), G. J. Mulder (Scheik. Verhandel. en Onderzoek ii. deel. 2, stuk. Ondez. 289), A. W. Hofmann (Quart. Journ. C. S. 11, 30), Berthelot (Compt. rend. 48, 469), Erlenmeyer (Annal. d. Chem. u. Pharm. 139, 17; also Zeitschr. f. anal. Chem. 6, 110), Leopolder (Zeitschr. f. anal. Chem. 8, 198), Donny (*Ib.* 118, 200), Glaser (Annal. d. Chem. u. Pharm. Suppl. 7, 213; also Zeitschr. f. anal. Chem. 9, 392).

‡ Comp. das Preisverzeichniss der Bunsen'schen Apparate vom Universitätsmechanikus Desaga in Heidelberg, 1873, p. 36.

§ Annal. d. Chem. u. Pharm. 139, 70; Zeitschr. f. anal. Chem. 6, 110.

Löwe's recommendation, with several small openings. Löwe * also provides a clay channel above the combustion tube, so that the latter is surrounded by clay.

The heat is confined and reverberated by fire-clay tiles, which are placed on both sides, and together form a roof; those on one side are fixed, on the other movable. The tube in which the burners are screwed, and also the iron channels in which the fire-bricks lie, can be raised or lowered, so as to suit combustion tubes of various sizes, and to enable the operator to regulate the distance between the burners and the trough containing the combustion tube.

Heintz's apparatus is also said to be excellent. It will be found figured in Hugershoff's price-list (Leipsig, 1874, p. 55). I cannot speak from my own experience in this matter. A. W. Hofmann's furnace † differs materially from the above in its construction; it was much used in England, and can be recommended, but it consumes a larger quantity of gas. It is constructed as follows :—

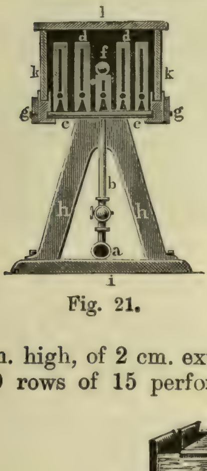

Fig. 21.

Into the horizontal brass tube *a* (fig. 21), which is about 90 cm. long and 2 cm. thick, and is connected at both ends with the service of gas, there are screwed 30 to 34 upright tubes (*b*). These tubes are 30 cm. high and 1 cm. thick, each being provided with a stop-cock, and bears a cross-tube (*c c*) 15 cm. long and 1·5 cm. thick. Into each cross tube are screwed 5 ordinary fish-tail burners (each consuming 4 cubic feet of gas per hour for a full luminous effect), on which a corresponding number of clay burners fit loosely. These latter are well-burnt hollow cylinders of ordinary pipe-clay, or similar material, closed at the top, the sides being perforated with pin-holes. The tall outside cylinders (in 2 double rows) are 8·5 cm. high, of 2 cm. external and 1 cm. internal diameter; each contains 10 rows of 15 perforations each. The short middle cylinders (in a single row) differ from the others in being 4·5 cm. high, and, containing 70 to 80 perforations, they serve as a support for the combustion tube (*f*), which is thus bedded in a channel of heated fire-clay. An iron

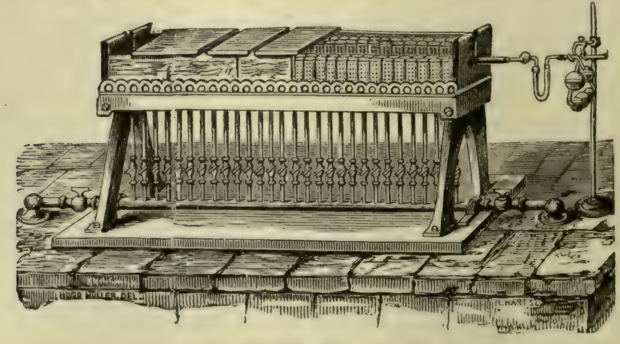
HUGO MÜLLER DEL.
R. HART SC.

Fig. 22.

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* Zeitschr. f. anal. Chem. 9, 222.

† Quart. Journ. Chem. Soc. 11, 30.

frame imparts the requisite amount of stability to the whole system. The side plates of clay (*k k*) are movable, and stand in a groove, thus overtopping the cylinders by 1·5 cm., although they are of the same height; movable clay-covers (*l*) are laid on the side plates. Fig. 22 is a drawing of the complete furnace. In the fore-part, the side plate and covers are removed, so as to show the disposition of the clay burners.

During the combustion, all the clay burners are enclosed as shown in the left-hand part of fig. 22. The most appropriate interval between the several burners is 3 mm. It is very important, in order to attain a perfectly uniform temperature, that the several arms bearing the burners should be equidistant. Their position is therefore specially secured by corresponding holes in the iron frame.

Finally, a furnace may here be mentioned which has been constructed on DONNY'S principle by C. GLASER in conjunction with KEKULÉ. This, like HOFMANN'S, saves the combustion tubes, but also consumes more gas than ERLENMEYER'S. Its characteristic feature is that the combustion tube rests on a series of iron supports pierced with holes, which are surmounted by perforated clay covers. The hot gases from the flame, which first heat the iron supports of the tube, are compelled to pass through the two systems of openings, and the tube is thus heated on all sides, and especially from above. The iron supports are movable, so that, if it is desired to lower the heat, they may be separated from each other by small intervals. The furnace is made by G. GERHARDT, at Bonn. It is particularly adapted for use with a current of oxygen, and its detailed description will therefore be deferred to § 178.

II. Performance of the Analytical Process.

a. The potash bulbs are first weighed, then the chloride of calcium tube; about ·35—·6 grm. of the substance under examination (more or less, according as it is rich or poor in oxygen) is introduced into the weighing-tube, which must be no longer warm, care being taken that no particles of the substance adhere to the sides of the tube, at least at the top; the stopper is then accurately inserted, and the tube and its contents weighed. The weight of the empty tube being approximately known, it is easy to take the right quantity of substance required for the analysis.

b. The sheet of glazed paper is spread upon a clean table, and the still moderately warm mortar placed upon it. Both the mortar and the still warm combustion tube are rinsed with a little of the warm oxide of copper;* the combustion tube is then filled up to *b* (fig. 23) with oxide of copper, either using the tube itself to take up the oxide with, or transferring the latter from the crucible to the tube with the aid of a small warm copper funnel and a teaspoon of German silver. A portion

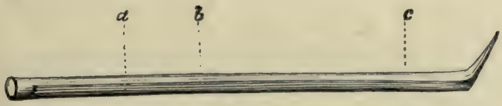

Fig. 23.

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* The oxide which has served for this purpose is put by.

of the oxide of copper is transferred from the tube to the mortar, the substance intended for analysis added from the small tube in which it has been weighed, taking care to shake out, as far as practicable, the last adhering particles of the substance; the stopper is then replaced, and the tube put by carefully, as it must be reweighed. The substance and the oxide is mixed in the mortar most intimately, taking care to avoid a too energetic pressure on the pestle; nearly all the oxide of copper still in the tube is added to the mixture, leaving only a layer of about 3 or 4 cm. in the latter; and the whole mixed together. The pestle is taken out of the mortar, shaking off as much as possible the minute particles of the mixture adhering to it; the greater part of the contents of the mortar is transferred to the tube, employing the latter itself for the purpose, and the rest of the mixture is shaken out on to a smooth card, and from this into the tube; the mortar is rinsed with a little more oxide of copper from the crucible, and this also is put into the tube, which will now be full to about *a* (fig. 23); fill up to within 3 or 4 cm. from the mouth with pure oxide of copper from the crucible, insert a plug of copper turnings oxidized by ignition in the air, and close the tube temporarily with a cork. The reason why the operation of filling the tube is conducted over the sheet of glazed paper is that, should any of the mixture be spilled, this may be readily recovered.*

c. A few gentle taps on the table will generally suffice to shake together the contents of the tube, so as to completely clear the tail from oxide of copper, and leave a free passage for the evolved gases from end to end, as shown in the cut. Should this fail, as will occasionally happen, owing to malformation of the tail, the object in view may be attained by striking the mouth of the tube several times against the side of a table. The tube is now placed in the wooden trough *D* (fig. 24), connected by a cork with the chloride of calcium tube *B*, and the latter again with an air-pump. The combustion tube is surrounded throughout its length with hot sand, and the air pumped out *slowly* (quick and incautious pumping might cause a portion of the mixture to pass into the chloride of calcium tube); the stop-cock *a* is then opened to admit a fresh supply of air, which is completely dried in its passage through the chloride of calcium tube; the tube is again exhausted, fresh air readmitted, and this process of alternate exhaustion and readmission of air repeated 10 or 12 times, to insure the perfect removal of the moisture which the oxide of copper may have absorbed during the operation of mixing. If a water-pump is used instead of a syringe, insert between it and the chloride of calcium tube a fork-shaped tube (fig. 25), connecting *a* with the chloride of calcium tube, *b* with the water-pump, and close *c* with a piece of flexible tube and a clip. After each exhaustion admit fresh air by *c*.

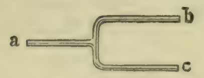

Fig. 25.

d. The end *b* (fig. 26) of the weighed chloride of calcium tube is connected with the combustion tube by means of a dried perforated cork, the furnace laid upon its supports, with a slight inclination forward, and the combustion tube placed in it; the other end of the chloride of calcium tube is connected by means of a vulcanized india-rubber tube with the end *m* of the potash apparatus, and, if necessary, secured with silk cord, taking care to press the knuckles of the two thumbs close together whilst tightening the cords, otherwise, should one of the cords happen to give way, the whole apparatus might be broken; the potash apparatus rests on a folded piece of cloth. Fig. 26 shows the whole arrangement.

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* In G. J. Mulder's laboratory I saw the operation of filling performed in a different, but certainly not less judicious way. The combustion tube was placed upright in a retort holder, and the mixture, which had been made in a small copper dish, filled in through a smooth, warm copper funnel. The anterior part of the tube is filled with granulated oxide of copper, in a tightly packed layer of at least 20 cm., and the carrying away of any oxide by the gases is provided against by a plug of copper turnings. Comp. Zeitschr. f. anal. Chem. 1, 7.

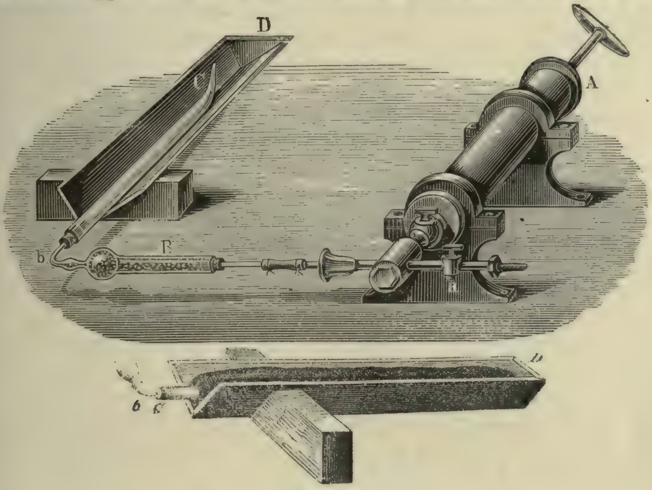

Fig. 24.

e. To ascertain whether the joints of the apparatus are air-tight, a piece of wood about the thickness of one's finger (*s*), or a cork or other body of the kind is put under the bulb *r* of the potash apparatus, so as to raise that bulb slightly; the bulb *m* is heated by holding a piece of red-hot charcoal near it, until some of the air is driven out of the apparatus, the piece of wood (*s*) is then removed, and the bulb *m* allowed to cool. The solution of potassa will now rise into the bulb *m*, filling it more or less; if the liquid in *m* remains for the space of a few minutes at the same level as it assumes after the perfect cooling of the bulb, the joints may be considered perfect; should the liquid, on the other hand, gradually regain its original level in both limbs of the apparatus, this is

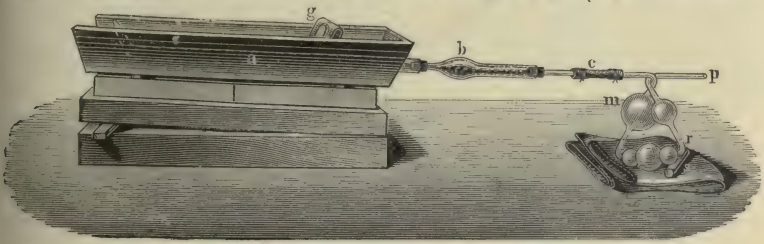

Fig. 26.

a sure sign that the joints are not air-tight. (The few minutes which elapse between the two observations may be advantageously employed in reweighing the little tube in which the substance intended for analysis was originally weighed.)

f. The mouth of the combustion tube should project 3 or 4 cm. beyond the furnace; the single screen is placed over the fore-part of the furnace, as a protection to the cork; the double screen is put over the combustion tube about 6 cm. farther on (see fig. 26), the little piece of wood (*s*) replaced under *r*, and small pieces of red-hot charcoal put first under that portion of the tube which is between the screen and the front; this portion is gradually surrounded with ignited charcoal, and allowed to get red-hot;* the screen is then shifted 3 cm. farther back, the newly exposed portion of the tube also surrounded with ignited charcoal, and allowed to get red-hot; and proceed in this manner slowly and gradually extending the application of heat to the tail of the tube, taking care to wait always until the last exposed portion is red-hot before shifting the screen, and also to keep the whole of the exposed portion of the tube before the screen in a state of ignition, and the projecting part of it so hot that the fingers can hardly bear the shortest contact with it. The whole process generally requires from ¾ to 1 hour. It is quite superfluous, and even injudicious, to fan the charcoal constantly; —this should be done, however, when the process is drawing to an end, as we shall see presently.

The liquid in the potash bulbs is gradually displaced from the bulb *m* as the fore-part of the combustion tube becomes heated, owing to the expansion of the heated air. When the heat reaches the oxide of copper used to rinse the mortar, a little carbonic acid and aqueous vapor are evolved, which drive before them the air in the apparatus, and force it in large bubbles through the potash bulbs, but as soon as the heat reaches the actual mixture the evolution of gas proceeds with greater briskness; the first bubbles are only partly absorbed, as the carbonic acid is still mixed with air; but those which follow are so completely absorbed by the potassa that merely a solitary air-bubble escapes through the liquid from time to time. The combustion is carried on so as to make the gas-bubbles follow each other at intervals of from ½ to 1 second.

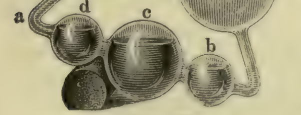

Fig. 27.

Fig. 27 shows the proper position of the potash bulbs during the operation. It will be seen from this that an air-bubble entering through *m* passes first into the bulb *b*, thence to *c*, from *c* to *d*, and, passing over the solution in the latter, finally escapes into the bulb *f*, through the fluid which just covers the mouth of the tube *e*.

g. When the tube is surrounded with red-hot charcoal throughout its whole length, and the evolution of gas diminishes, the burning charcoal should be gently fanned with a piece of pasteboard. When the evolution of gas has entirely ceased, the position of the potash bulbs must be adjusted to a level, the charcoal removed from the farther end of the tube, and the screen placed before the tail. The cooling of the tube which takes place on the one hand, and the absorption of the carbonic acid in the potash bulbs on the other, cause the solution of potassa in the latter to recede, slowly at first, but with increased rapidity from the moment the liquid reaches the bulb *m*. (If care is taken to properly adjust the potash bulbs, there is no fear that the contents of the latter will run back into the chloride of calcium tube.) When the bulb *m* is about half filled with solution of potassa, the point of the combustion tube is broken off with a pair of pliers or scissors, whereupon the fluid in the potash bulbs will immediately resume its level. The potash bulbs are now restored to their original oblique position, and the glass tube mentioned § 174, 10, placed over the tail, supporting it against the arm of a filtering stand; wait a few minutes, so that the carbonic acid in the chloride of calcium tube and the combustion tube may be absorbed by the potash, then suck air slowly through the potash bulbs, by means of the suction tube, or a caoutchouc tube, until the bubbles passing through no longer diminish in size. Fig. 28 shows the arrangement of the apparatus at this juncture.

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* In using a gas furnace, of course the burners are lighted one after another.

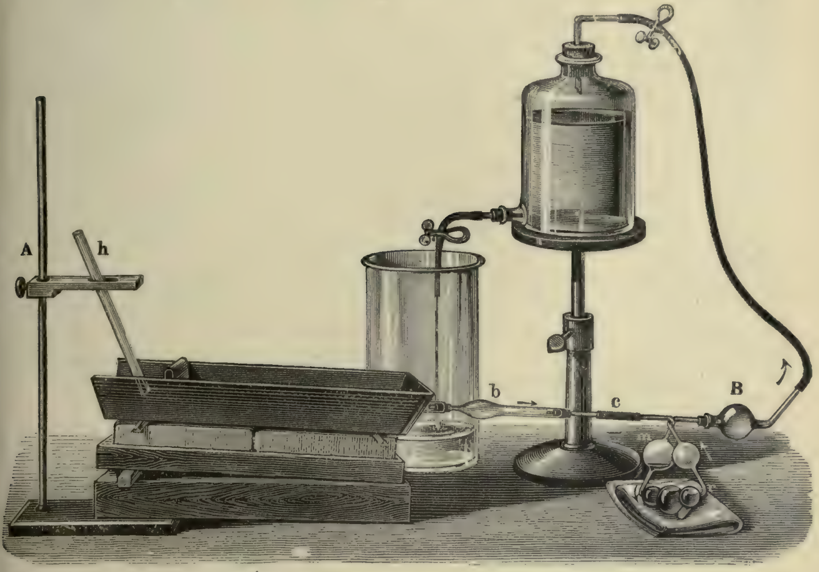

Fig. 28.

It is better to employ a small aspirator instead of sucking with the mouth, as the volume of air that has passed through the apparatus is then accurately known. Liebig directed not to draw more air through than a quantity equal to the contents of the chloride of calcium tube and the combustion tube—about 80 or 100 cc. In fact, if the simple Liebig's arrangement is adopted, it would not be safe to exceed this quantity, as errors would be introduced.

This terminates the analytical process. The potash bulbs are disconnected, and the chloride of calcium tube removed from the combustion tube, together with the cork, which should not be charred. The cork is then removed from the chloride of calcium tube, and the apparatus allowed to cool. After half an hour * the potash bulbs and the chloride of calcium tube are weighed, and the results calculated: they are generally very satisfactory. The carbon is usually accurate, but somewhat too low (about ·1 per cent.) rather than too high. The carbon determination, indeed, is not free from sources of error; but none of these interfere materially with the accuracy of the results, and the deficiency arising from the one is partially balanced by the excess arising from the other. In the first place, the air which passes through the solution of potassa during the combustion, and afterwards during the process of suction, carries away with it a trace of moisture. This loss is increased if the evolution of gas proceeds very briskly, as it tends to heat the solution of potassa; and also if nitrogen or oxygen passes through the potash bulbs (compare § 178 and § 183): this may be avoided, however, by fixing to the exit end of the latter a tube with solid hydrate of potassa, the bulbs and this tube being always weighed together. In the second place, traces of carbonic acid from the atmosphere are carried into the potash apparatus in the final process of suction; this may be remedied by connecting the tail of the combustion tube, during the operation, with a tube containing hydrate of potassa by means of a perforated cork or flexible tube. Thirdly, in the analysis of substances containing a considerable proportion of water or of hydrogen, it frequently happens that the carbonic acid is not sufficiently dried in passing through the chloride of calcium tube; this source of error may be avoided by substituting an apparatus containing sulphuric acid, for the chloride of calcium tube (compare § 182).

The hydrogen is usually somewhat too high, on an average from ·1 to ·15 per cent.; this arises principally from the circumstance that the air passing through the apparatus during the final process of suction conveys a little moisture into the chloride of calcium tube; but this may be readily remedied by connecting the tail of the combustion tube with a tube containing hydrate of potassa.

I must, however, expressly remark that, in most cases, it is quite unnecessary to make the operation more complicated simply for the purpose of correcting these defects, especially as we know from innumerable experiments the influence they have on the results.

2. BUNSEN'S MODIFICATION OF LIEBIG'S METHOD.†

§ 175.

The essential points of this modification are, that the oxide of copper is allowed to cool in a closed tube, or flask, and that, instead of being mixed with the substance in a mortar, it is transferred at once to the combustion tube, and the operation of mixing effected in the latter; by these means the absorption of moisture from the air is effectually guarded against, and the exhaustion of the tube is dispensed with.

This modified process is more particularly suitable for the analysis

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* LÖWE considers that half an hour is not enough, at least when his very concentrated potash is used in the bulbs. He says the weight is not constant until after the lapse of two or three hours. The open ends of the apparatus are closed during the cooling (not the weighing) by fragments of flexible tube and pieces of glass rod.

† KOLBE, Handwörterbuch der Chemie, Supplemente, 186; A. STRECKER, *Ib.* 2nd edition, I. 852.

of highly hygroscopic bodies and substances which cannot well be mixed with warm oxide of copper without risk of decomposition.

The dried substance is weighed in a tube of thin glass, about 20 cm. long, and of about 7 mm. bore; one end of this tube is closed by fusion, the other, during the operation of weighing, with a smooth cork.

Besides this weighing-tube, BUNSEN's method, like LIEBIG's, requires a combustion tube, potash bulbs, chloride of calcium tube, connecting tube of india-rubber, perforated cork, suction tube, combustion furnace, and oxide of copper (see § 174); and, in addition to these, a wide glass tube sealed at one end, or a flask (fig. 29), in which the freshly ignited oxide of copper is allowed to cool, and from which it is transferred to the combustion tube, secure from the possible absorption of moisture from the air.

The freshly ignited and still quite hot oxide of copper is transferred direct from the crucible to this filling tube, or flask, which is then closed air-tight with a cork. It saves time to fill in at once a sufficient quantity of oxide to last for several analyses. If the cork fits tightly, the contents will remain several days fit for use, even if a portion has been taken out and the tube repeatedly opened.

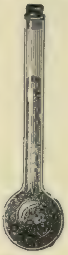

Fig. 29.

The filling of the combustion tube is effected as follows:—The perfectly dry tube is rinsed with some oxide of copper; a layer of oxide of copper, about 10 cm. long, is introduced into the posterior end of the combustion tube, by inserting the latter into the filling tube, or flask, containing the oxide of copper (fig. 30), holding both tubes in an oblique direction, and giving a few gentle taps.

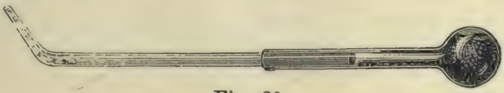

Fig. 30.

The tube with the substance must be accurately weighed shortly before, together with the cork. After removing the cork cautiously, to prevent the slightest loss of substance, the open end of the tube is inserted as deep as possible into the combustion tube, and the requisite quantity of substance poured from it, by giving it a few turns, pressing the rim all the while gently against the upper side of the combustion tube, to prevent its coming into contact with the powder already poured out; the two tubes are, in this manipulation, held slighly inclined (see fig. 31).

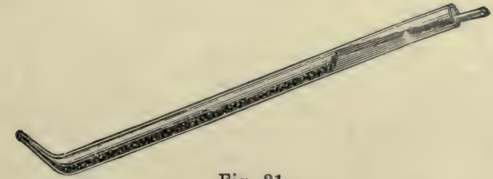

Fig. 31.

When a sufficient quantity of the substance has been thus transferred from the weighing to the combustion tube, the latter is restored to the horizontal position, which gives to the former a gentle inclination with the closed end downwards. If the little tube is now slowly withdrawn, with a few turns, the powder in the tube near the mouth falls back into it, leaving the opening free for the cork. The tube is then immediately corked and weighed, the combustion tube being meanwhile kept closed with a cork. The difference between the two weighings shows the quantity of substance transferred from the weighing to the combustion tube. The latter is then again opened, and a quantity of oxide of copper, equal to the first, transferred to it from the filling tube, or flask, taking care to rinse down with this the particles of the substance still adhering to the sides of the tube. There is now in the hinder part of the tube a layer of oxide of copper, about 20 cm. long, with the substance in the middle.

The next operation is the mixing : this is performed with the aid of a long polished brass or iron wire, with a ring for a handle at one end, and pointed and twisted corkscrew fashion (with a single twist) at the other (see fig. 32).

Fig. 32.

The wire is pushed rapidly up and down the tube with a slight screwing motion. A few minutes suffice to effect perfect intermixture ; so perfect, indeed, in the case of pulverulent substances which do not cake, that the minutest particles can no longer be distinguished with the naked eye. The combustion is effected as in § 174.

β. Difficultly combustible non-volatile bodies—e.g., resinous and extractive matters, coal, &c.

If substances of the kind are analysed by the methods given in §§ 174 and 175, minute particles of carbon are liable to escape combustion. To prevent this, one of the following methods is resorted to : these may also be used for readily combustible bodies.

1. Combustion with Chromate of Lead, or with Chromate of Lead and Dichromate of Potassa, or with Chlorate of Potassa and Oxide of Copper.

§ 176.

When chromate of lead is used alone, all the apparatus, &c., enumerated in § 174 will be required except oxide of copper, which is here replaced by chromate of lead (§ 66, 2). A narrow combustion tube may be selected, as chromate of lead contains a much larger amount of available oxygen in an equal volume than oxide of copper. A quantity of the chromate, more than sufficient to fill the combustion tube, is heated in a platinum or porcelain dish over a gas or Berzelius lamp, until it begins to turn brown; before filling it into the tube, it is allowed to cool down to 100°, or a little below. The process is conducted precisely as that described in § 174. It was formerly believed that when chromate of lead was used the application of the exhausting syringe to the warmed tube might be omitted, as the lead salt was considered to be non-hygroscopic, or at all events far less hygroscopic than the oxide of copper. But since Erdmann* has shown that this opinion is unfounded, and that, on the contrary, chromate of lead attracts moisture quite as rapidly as oxide of copper, there is no longer any reason for neglecting the exhaustion.

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* Journ. f. prakt. Chem. 81, 180.

As one of the principal advantages which chromate of lead has over oxide of copper as an oxidizing agent is its property of fusing when strongly heated, the temperature in the last stage of the process of combustion must be raised (by fanning the charcoal, &c.) sufficiently high to completely fuse the contents of the tube, as far as the substance extends. To heat the fore part of the tube to the same degree of intensity would be injudicious, as the chromate of lead in that part would lose all porosity, and thus also the power of effecting the combustion of the products of decomposition which may have escaped oxidation in the other parts of the tube.

As the chromate of lead, even in powder, is, on account of its density, by no means all that could be desired in this latter respect, it is preferable to replace the chromate of lead in the fore part of the tube, by coarsely pulverized strongly ignited oxide of copper, or with copper turnings which have been superficially oxidized by ignition in a muffle or in a crucible with access of air.

In the case of very difficultly combustible substances—such as graphite—it is desirable that the mass should not only readily cake, but also, in the last stage of the process, give out a little more oxygen than chromate of lead does. It is therefore advisable in such cases to add to the latter one-tenth of its weight of fused and powdered dichromate of potassa; in this way even very difficultly combustible bodies may be completely oxidized (LIEBIG*).

Good results may also be obtained by the use of oxide of copper and dichromate of potassa. GINTL† recommends the following manner of operating, which is very similar to BUNSEN'S. A 6 cm. layer of coarse oxide of copper is first put into the combustion tube, then 3 cm. of the dichromate which has been fused, pulverized, and preserved out of contact with air, then the substance, then again 3 cm. oxide of copper. Mix with the wire, taking care that 3 cm. of oxide of copper remains at the end of the tube free from chromate. Finally the tube is fully charged with oxide of copper in the usual way, and the combustion commenced. As the potash takes up oxygen towards the end, a little more air free from carbonic acid and water must be passed through the apparatus at the close of the operation. The exit of the potash bulbs must be connected with a tube two-thirds filled with soda-lime and one-third with chloride of calcium, which is weighed with the bulbs.

2. COMBUSTION WITH OXIDE OF COPPER AND CHLORATE OR PERCHLORATE OF POTASSA.

§ 177.

This method requires the whole of the apparatus, &c., enumerated in § 174 or § 175, and, in addition, a small quantity of chlorate of potassa; this is freed from water by heating it until it fuses, allowing it to cool, and then reducing it to a coarse powder, which is kept in a warm place until required for use.

The process is conducted as in § 174 or § 175, with this difference, that the layer of oxide of copper in the posterior end of the tube is made about 5 cm. long, instead of 3 or 4, and is mixed by agitation with about one-eighth (3 or 4 grams) of chlorate of potassa; a layer of 2 cm. of pure oxide of copper is placed between this mixture and that which contains the substance to be analysed. When, in the subsequent heating of the tube, the part occupied by the mixture containing the chlorate of potassa is approached, the greatest caution must be used in laying on the charcoal or turning on the gas, so as to insure the very gradual decomposition of the chlorate; for if this precaution is neglected, the impetuous rush of the gas will eject a small portion of the solution of potassa, thus vitiating the analysis altogether.

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* MAYER has published a series of most successful experiments made with this excellent method (Annal. d. Chem. u. Pharm. 95, 204).

† Zeitschr. f. anal. Chem. 7, 302.

The oxygen liberated from the chlorate of potassa drives the carbonic acid before it, effects the combustion of the unconsumed particles of carbon, and oxidizes the reduced copper. Oxygen gas therefore cannot escape through the potash bulbs until all that is oxidizable in the tube has been oxidized.

If, in the last stage of the combustion, a large quantity of gas has in this way passed unabsorbed through the potash bulbs, it is unnecessary to break off the point, and draw air through the combustion tube, as the latter now contains nothing but oxygen, and neither carbonic acid nor aqueous vapor. But air dried and freed from carbonic acid must be drawn through the chloride of calcium tube and the potash bulbs, as these parts of the apparatus would otherwise be weighed full of oxygen.

As chlorate of potassa decomposes with a certain degree of violence, which is not the case with *perchlorate of potassa*, the latter salt, prepared by heating the former, may be used in preference, as BUNSEN has proposed. The fused and still hot perchlorate is introduced into the farther end of the tube, a loose plug of recently ignited asbestos is inserted, and the tube then filled in the usual way. If BUNSEN's mode of mixing (§ 175) is adopted, an asbestos plug must always be used (also when the chlorate is employed), so that in the mixing the substance may be kept from coming into immediate contact with the salt which yields the oxygen.

As the dry oxygen gas passing through the potash bulbs carries away a little aqueous vapor from the solution of potassa, it is advisable to connect the exit tube of the bulbs by a cork, or a tube of india-rubber, with a small tube filled two-thirds with soda-lime and one-third with chloride of calcium, the bulbs and this little supplementary tube being always weighed together.

3. COMBUSTION WITH OXIDE OF COPPER AND OXYGEN GAS.

§ 178.

In the analysis of organic bodies, many chemists deviate from the methods described in the preceding paragraphs, and effect the combustion with oxide of copper and oxygen gas supplied by a gasometer. HESS, DUMAS and STAS, ERDMANN and MARCHAND, PIRIA, STRECKER, WÖHLER, LÖWE, GLASER, and others have proposed methods founded on this principle, which they employ not only for the analysis of difficultly combustible bodies, but also to effect the determination of the carbon and hydrogen in organic substances in general. These processes, as well as the others, have been in use in the author's laboratory for many years.

As these methods require a gasometer filled with oxygen, also certain arrangements to dry the oxygen completely, and to free it from carbonic acid, it is evident that the apparatus must be more complicated than LIEBIG'S or BUNSEN'S. They are chiefly useful in cases where a number of ultimate analyses have to be made in succession; and also more particularly in the analysis of substances which cannot be reduced to powder, and consequently do not admit of intimate mixture with the oxide of copper.

HESS, and ERDMANN and MARCHAND, used spirit of wine to heat the combustion tube, but since the introduction of gas into laboratories these furnaces are scarcely ever used. The charcoal furnace shown in fig. 17, p. 12, may be used for this purpose, but it will require to be 70 or 80 cm. long. The manner of heating has no influence on the operation, or on the accuracy of the results, provided that the heat can be regulated at will, and carried to the necessary degree of intensity.

Combustion with the aid of oxygen gas may be carried out in two ways, according as the substance is mixed with oxide of copper, or not. The latter, in which the substance is placed in a boat in the combustion tube, is the most convenient of all methods, for, as soon as one analysis is ended, the combustion tube is quite ready for the next. This method is described under *a*. The other method, in which the substance is mixed with oxide of copper, will be given under *b*.

a. Combustion in a boat.

As it is of the utmost importance in this method to be able to use the same combustible tube over and over again, a gas furnace should be used, which favours the preservation of the tubes—viz., either GLASER'S improvement of DONNY'S furnace, or HOFMANN'S.

Fig. 33 (next page) shows the whole apparatus, as described by GLASER.*

At the ends of the furnace are two iron upright supports, screwed on an iron plate. Between these run two parallel iron bands; and perpendicularly over the latter are two iron rods, also fixed into the upright supports. The bricks are grooved at the top and bottom, and are kept in place between the bands and the rods. They are readily movable from side to side, and serve, as shown in the section (fig. 34), as supports for the iron bed, which is made in sections. One of these sections is shown at the right lying down in fig. 33. The hot gases from the burners below the iron bed pass through the openings in the latter, are reverberated on the combustion tube, and then escape through the openings of the clay covers (fig. 34). By this arrangement the important result is attained, that the tube is heated more especially from above and from the sides, as in LIEBIG'S charcoal furnace. (In ordinary combustions, two or three of the sections of the bed are separated from the rest at the spot where the mixture of oxide with the substance lies. As the combustion progresses, these sections

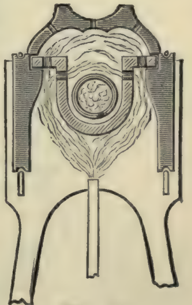

Fig. 34.

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* Annal. d. Chem. u. Pharm. Supplementb. 7, 213; also Zeitschr. f. anal. Chem. 9, 392. The apparatus may be obtained from MARQUART, of Bonn.

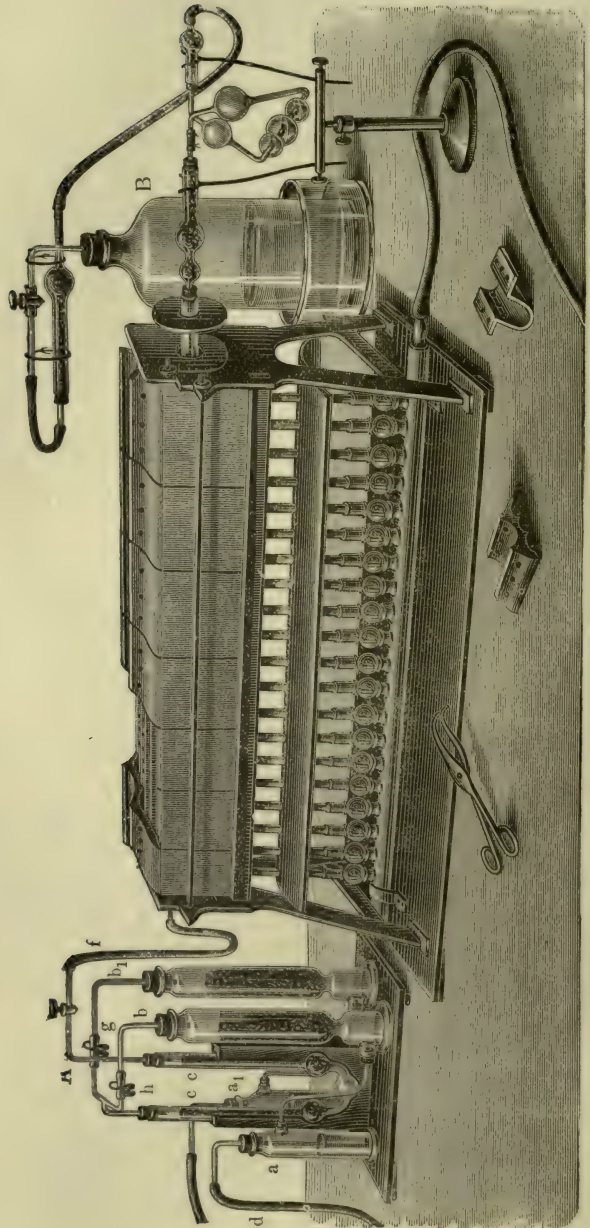

Fig. 33.

may be readily pushed towards the others; the combustion tube, which is in a channel of wire gauze, being firmly held the while with one hand.

The combustion tube (fig. 35) is open at both ends. From *a* to *b*, it contains oxidized copper turnings and granulated oxide of copper, kept in place by stoppers of copper gauze * at *a* and *b*. *b c* contains a spiral of oxidized copper, made from rolled copper gauze. (In the analysis of substances which contain chlorine, bromine, or nitrogen, a spiral of metallic copper is substituted for this; see below.) The part *a d* contains the substance in a platinum boat; *d e* contains a spiral of metallic copper fastened to a wire. The tube rests in a channel of wire gauze on the bed of the furnace, three of the sections of the bed being removed at the spot under the platinum boat; the fore part of the tube is connected with an unweighed chloride of calcium tube, the other end with the purifying and drying apparatus and the gasometers. *a* and a_1 contain solution of potash, the first being connected by *d* with a gasometer containing oxygen, the second by *l* with a gasometer containing air; *b* and b_1 are filled with soda-lime in the lower two-thirds, and the upper third with chloride of calcium. The U tube *c c*, through which oxygen or air passes into the combustion tube, contains chloride of calcium. It is connected with the combustion tube by a glass tube provided with a stopcock, and the flexible tube *f*.

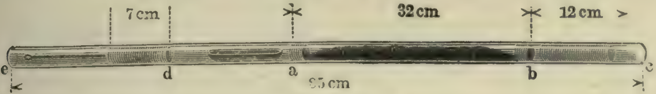

Fig. 35.

In order to obviate the possibility of a diffusion of the products of combustion of the substance into the drying tubes, Löwe † inserts a mercurial valve between the chloride of calcium tube of the drying apparatus and the combustion tube, as in fig. 36. The air or oxygen enters at *a* and passes out at *b*. In the point of the tube *c* is a small quantity of mercury, into which the tube *a*, which is drawn out to a point, dips. The india-rubber stopper in *c* is covered with gelatine solution to insure its being air-tight.

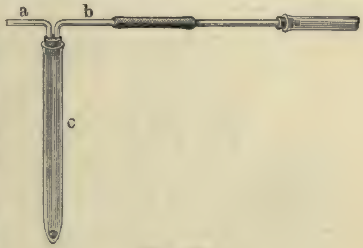

Fig. 36.

In making an analysis, the tube is first heated from end to end, passing all the time a gentle current of dry air through it, and is then allowed to cool. The posterior copper spiral in the hinder part of the tube is then taken out, and the boat, with the substance, inserted, the spiral replaced, and after putting on the iron disc seen fig. 33, or one of clay (Löwe), the fore part of the combustion tube is connected with the absorption apparatus. The guard tube connected with the aspirator *B* by a stopcock is not weighed; it contains chloride of calcium in the bulb and the half near it, soda-lime in the other half. The aspirator consists of a tubulated bell standing in dish filled with water. The stop-cock being opened, the water is sucked into the bell, until the difference of level is about 12 or 15 cm. This aspirator, which PIRIA* first described, serves to counterbalance the pressure in the combustion tube caused by the potash bulbs, and also offers a convenient means of testing the tightness of the whole apparatus.

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* Löwe (Zeitschr. f. anal. Chem. 9, 218) uses instead hemispheres of rather coarse platinum gauge, whose convex surfaces are turned towards the absorption apparatus.

† Zeitschr. f. anal. Chem. 11, 407.

Having thus got everything ready, the glass stop-cock of the drying apparatus is closed, that of the aspirator opened, and the front part of the combustion tube and the hinder copper spiral are heated to low redness; the cock of the drying apparatus is then opened, and a very slow current of oxygen allowed to pass, which, however, will be entirely absorbed by the copper spiral in *d e*, and merely serves to prevent the products of combustion from entering the hinder part of the tube.

The substance is now heated either directly or by radiant heat according to its degree of volatility, the temperature being easily regulated by means of the movable clay covers. When at last nothing but carbon remains in the boat, the copper spiral in *e d* is allowed to cool, and a more rapid current of oxygen is passed to complete the combustion, and reoxidize the reduced copper. This oxidation is finished in a current of air which also serves to sweep out the oxygen from the whole apparatus. The gas is then turned off, the cock of the aspirator closed, the latter is disconnected from the absorption apparatus, and the potash bulbs and chloride of calcium tube weighed when cool.

A special paragraph, § 192, is reserved for the description of CLOEZ's method.

b. Combustion of the substance mixed with oxide of copper.

This method requires a tube about 50 cm. long, sealed behind, and drawn out as shown in fig. 37.

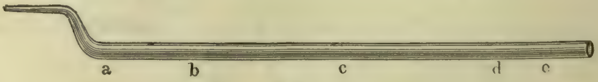

Fig. 37.

The operations are at first almost exactly the same as in BUNSEN's method (§ 175). The hinder part of the tube from *a* to *b* is filled with ignited granular oxide of copper, *b c* contains the substance mixed with ignited powdered oxide of copper by means of the wire, *c d* ignited granular oxide of copper, and *d e* an ignited spiral of copper gauze.

The combustion is conducted as usual, proceeding from the front to the back, but, before the mixture of the substance is reached, *a b* is heated to low redness to burn any products of distillation which may have passed backwards. When the whole tube is at a low red-heat and the evolution of gas has stopped, the hinder portion of the tube is allowed to cool somewhat, so that the point may be conveniently handled, and is then connected with the chloride of calcium tube, *c c*, of the purifying and drying apparatus, fig. 33, by means of a piece of india-rubber tube. The point of the combustion tube is now broken off in the connecting tube, and the combustion completed in a gentle current of oxygen, the oxygen being subsequently displaced by a gentle current of air; then allow to cool and weigh the absorption apparatus.

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* Cimento, 5, 321; Jahresber. von. KOPP u. WILL, 1857, 573.

γ. *Hygroscopic substances, volatile bodies, or such as suffer change—e.g., lose water at* 100°.

§ 179.

aa. Hygroscopic substances, if burnt in any of the ways already described, are liable to give too much hydrogen. Stein* recommends the following process.

The method is that described § 178, *a*. To prevent conduction of heat, the part of the tube where the platinum boat containing the substance is situated is not supported by any foil or gauze. The substance is dried in the air or in a desiccator, and weighed in the boat. The tube having been heated and cooled again, and the apparatus proved to be tight, the boat is introduced, one or two burners, from 9 to 12 cm., behind the boat are lighted, and a gentle current of warm dry air passed over the substance. Usually water soon makes its appearance in the chloride of calcium tube, then disappears again after a time, and does not reappear if the current of air is heated a little higher and the bulb of the chloride of calcium tube is cooled with ether. The absorption apparatus is now removed, and, while it is being weighed, a gentle current of dry air, not heated, is passed through the apparatus. The weight of the potash bulbs with their potash or soda-lime tube shows whether any decomposition of the substance has taken place, and the increased weight of the chloride of calcium tube shows the amount of hygroscopic water present. If the drying in a current of warm air is repeated, and the chloride of calcium tube reweighed, it is easy to ascertain with certainty whether the substance has been completely dried; when this point is reached, the combustion may be commenced.

In cases where a higher temperature is necessary to expel chemically confined water, Stein suspends a piece of copper foil by four thin wires between the burners and the tube at the spot occupied by the boat, places a thermometer between, and lights a burner under the foil. The temperature within the tube will of course be somewhat lower than that indicated by the thermometer. As soon as the substance is dried, the gas is put out and the foil removed.

bb. Volatile substances, or such as suffer alteration at 100°—*e.g.*, lose water. If substances of this kind were analysed as directed in § 174, a portion of the substance or some water would escape on mixing with hot oxide of copper and the application of the exhausting syringe to the tube, surrounded as it is with hot sand; the results, therefore, could not possibly be accurate. If, on the other hand, the mixing were effected in the same way with cold oxide of copper, the mixture would absorb water.

The process is therefore conducted either according to § 175 or § 178. Ignited chromate of lead, cooled in a closed tube, may also be employed as oxidizing agent, the mixing being effected in the combustion tube by a wire.

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* **Zeitschr. f. anal. Chem. 5, 33.**

b. FLUID BODIES.

a. Volatile liquids (such as ethereal oils, alcohol, &c.).

§ 180.

1. The analysis of volatile fluids requires all the apparatus enumerated in § 174, with the exception of the apparatus for weighing, mixing, and exhausting. The combustion tube should be somewhat longer than is there mentioned; it should have a length of 50, 60, or 85 cm., according as the substance is less or more volatile. If the combustion is not effected in a current of oxygen according to § 178, *a*, the process also requires a filling tube, or flask, as described in § 175, for the temporary reception of the oxide of copper. Small glass bulbs are used for the reception of the liquid to be analysed; these are made in the following manner:—

A glass tube, about 30 cm. long and about 8 mm. wide, is drawn out as shown in fig. 38, fused off at *d*, and *A* expanded into a bulb, as shown in fig. 39. The bulb is then cut off at β. Another bulb is made in the same way, and a third and fourth, &c., taking care that the length of tube left is sufficient to prevent the moisture of the mouth from reaching the bulb. Two of these empty bulbs are accurately weighed, then filled with the liquid to be analysed, closed by fusion, and weighed again. The filling is effected by slightly heating the bulb over a lamp and immersing the point into the liquid to be analysed, part of which will now, upon cooling, enter the bulb. If the liquid is very volatile, the portion entering the still warm bulb becomes converted into vapor, which drives the liquid out again; but directly the vapor is recondensed, the bulb is filled more completely. If the liquid is of a less volatile nature, a small portion only will enter at first; in such cases, the bulb is heated again to convert what has entered into vapor, and the point is then again immersed into the fluid, which will now readily enter and fill the bulb. The excess of fluid is ejected from the neck of the little tube by a sudden jerk; the point of the capillary neck is then sealed in the blowpipe flame. The combustion tube is now prepared for the combustion by introducing into it, from the filling tube, or flask (§ 175), a layer of oxide of copper about 6 cm. in length. The middle of the neck of one of the bulbs is slightly scratched with a file, the pointed end is quickly broken off, and the bulb and end are dropped into the combustion tube (see fig. 40). Another layer of oxide of copper, about 6—9 cm. long, is then put in, and the other bulb introduced in the same manner as the first; and lastly the tube is nearly filled with oxide of copper. A few gentle taps upon the table suffice to clear a free passage for the gases evolved. (It is advisable to place in the foremost half of the combustion tube small lumps of oxide of copper [comp. § 66, 1, vol. I.], or super-

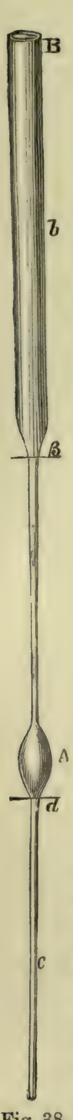

Fig. 38.

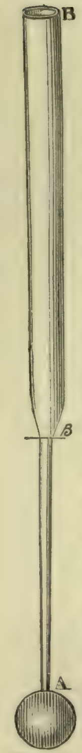

Fig. 39.

ficially oxidized copper turnings, or a mixture of such copper turnings with granular oxide of copper, so as to allow of the free passage of the gases, even when there is but a narrow channel, or no channel at all; for, with a wide channel, there is the risk of vapor passing unconsumed through the tube.)

The combustion of very volatile substances requires great care, and renders certain modifications of the common method necessary. In the first place, the foremost half of the tube is heated to redness; this is separated from the rest by a screen, or, in the case of highly volatile substances, by two screens; ignited charcoal is then placed behind the tube or a gas-burner lighted, to heat the tail and prevent the condensation of vapor in that part. A piece of red-hot charcoal, or a hot tile, is now applied to that part of the tube occupied by the first bulb; this causes the contents to flow out and evaporate; the vapor passing over the oxide of copper suffers combustion, and the evolution of gas commences, which is maintained by very gradually heating the first, and after this the second bulb; it is better to conduct the operation too slowly than too quickly. Sudden heating of the bulbs would at once cause such an impetuous rush of gas as to eject the fluid from the potash bulbs. Finally, the tube is heated throughout its entire length, and the rest of the operation conducted in the usual way. If the air drawn through the apparatus smells or tastes of the analysed substance, this is a sure sign that complete combustion has not been effected.

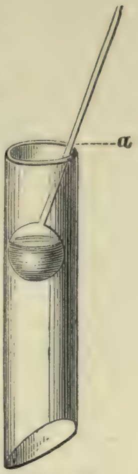

Fig. 40.

2. In the combustion of liquids of high boiling point and abounding in carbon—such as ethereal oils—unconsumed carbon is apt to be deposited on the completely reduced copper near the substance; it is therefore advisable to distribute the quantity intended for analysis (about ·4 grm.) in 3 bulbs, separated from each other in the tube by layers of oxide of copper.

3. In the combustion of less volatile liquids, it is advisable to empty the bulbs of their contents before the combustion begins: this is effected by connecting the filled tube with an exhausting syringe, and rarefying the air in the tube by a single pull of the handle; this will suffice to expand the air-bubble in each bulb sufficiently to expel the liquid from it, which is then absorbed by the oxide of copper.

4. If, as frequently happens, there is good reason to apprehend that the oxide of copper may not suffice to effect the complete combustion of the carbon, the process is terminated in a stream of oxygen gas which is passed, as in § 178, *b*, finally through the red-hot tube of the form shown in fig. 37, p. 28, or which is evolved from some chlorate or perchlorate of potassa in the hinder part of the tube (compare § 177).

5. If it is intended to effect the combustion in the apparatus described § 178, *a* (using a boat and a current of oxygen), the tube is prepared; the bulb or bulbs, with their points broken off, are placed in the boat, and introduced into the tube; the fore part of the latter is heated, then the hinder part, and the substance is thus evaporated and burnt in a slow current of warm air; then oxygen is passed, and finally again air. If this method is employed for very volatile liquids, such as ether, great caution is required, or an explosion may take place.

β. *Non-volatile Liquids* (*e.g., fatty oils*).

§ 181.

The combustion of non-volatile liquids is effected either (1) with chromate of lead, oxide of copper and chlorate or perchlorate of potassa, or finished in a current of oxygen according to § 178, *b*; or (2) in the apparatus described § 178, *a*.

1. The operation is carried out in general as directed §§ 176, 177, or 178, *b*. The substance is weighed in a small tube, placed for that purpose in a tin foot (see fig. 41), and the mixing effected as follows:—First a layer, about 6 cm. long, of oxide of copper—with or without the addition of chlorate of potassa—or chromate of lead is introduced into the combustion tube; then the small tube with the substance is dropped in, and the oil allowed to run completely out into the combustion tube; it should be made to spread about in various directions, taking care, however, to leave the upper side (intended for the channel) and the fore part, to the extent of a quarter or a third of the length of the tube, entirely clean. The tube is now nearly filled with oxide of copper or chromate of lead, which has previously been cooled in the filling tube, or flask—taking care that the small tube which contained the oil is completely filled with the oxidizing agent. The tube is placed in hot sand, which, imparting a high degree of fluidity to the oil, leads to the perfect absorption of the latter by the oxidizing agent; the exhausting syringe is applied, if necessary, and the combustion proceeded with in the usual way. It is advisable to employ a tolerably long tube. Chromate of lead is usually to be preferred; if it is used, a very intense heat, sufficiently strong to fuse the contents of the tube, is cautiously applied in the last stage of the process.

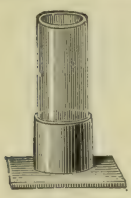
Fig. 41.

Solid fats or waxy substances which cannot be powdered and consequently cannot be mixed with the oxidizing agent in the usual way, are treated in a manner similar to fatty oils. They are fused in a small weighed glass boat (fig. 42), made of a tube divided lengthwise; when cold, the little boat with its contents is weighed, and then dropped into the combustion tube, previously filled to the extent of about 6 cm. with chromate of lead, or oxide of copper (in some cases mixed with chlorate of potassa). The substance is then melted and made to spread about in the tube in the same manner as is done with fatty oils, the rest of the operation being conducted exactly as in the latter case. If chromate of lead is employed, it will be found advantageous to add some dichromate of potassa (§ 176).

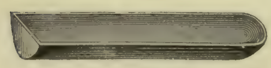
Fig. 42.

2. If it is intended to burn fatty substances or other bodies of the kind, in a current of oxygen gas, in the apparatus described in § 178, *a*, the substance is weighed in a porcelain, copper, or platinum boat, which is then inserted into the tube, prepared as usual. The combustion must be conducted with great care. As soon as the oxide of copper in the fore part of the tube and the copper spiral in the hinder part are red hot, a slow current of oxygen is passed, and a piece of red-hot charcoal, or a hot tile, is placed near the substance. The volatile products generated by the dry distillation burn at the expense of the oxide of

copper. When it is perceived that the surface layer of the oxide of copper is reduced, the application of heat to the substance is suspended for a time, and resumed only after the copper has become reoxidized in the stream of oxygen. Lastly, care must be taken to insure the complete combustion of the carbon remaining in the boat.

Supplement to A, §§ 174—181.*

§ 182.

Modified Apparatus.

1. *For connecting the chloride of calcium tube with the combustion tube.*

As is well known, Berzelius, unlike Liebig, did not connect the combustion tube with the chloride of calcium tube by a cork, but drew it out in front to a long point, which was first bent upwards at an obtuse angle, then downwards, and was finally fixed in the bulb of a peculiarly shaped chloride of calcium tube by an india-rubber bandage. This arrangement was inconvenient for tubes which were charged at the mouth. Löwe † now recommends a similar arrangement for tubes which are open behind. He draws out the front part to a point not too thin or narrow, which has a slight inclination near the orifice, and fixes this by means of an india-rubber stopper into the lateral tubulus of the bulb of a U-shaped chloride of calcium tube. Löwe claims this benefit, that the joint does not tend to loosen as the tube expands when heated, as is usually the case, but actually becomes tighter.

Al. Mitscherlich ‡ draws out the front of the combustion tube straight, and fixes the point by means of a ring of flexible tube into his apparatus for absorbing water (a tube of anhydrous phosphoric acid).

2. *For the absorption of water.*

Chloride of calcium is well known not to be adapted for completely drying moist gases; according to the author's experiments,§ it is surpassed in this respect by sulphuric acid, and this again, although to a very slight extent,|| by anhydrous phosphoric acid. Many chemists, therefore, use sulphuric acid instead of chloride of calcium. For this purpose the apparatus shown by figs. 13, 14, and 15, p. 10, may be used; the tubes are filled with fragments of ignited pumice or glass, moistened with pure sulphuric acid. Schrötter ¶ recommends the form shown in fig. 43. The two tubes contain pumice moistened with sulphuric acid, and the bulb contains a small quantity of the acid.

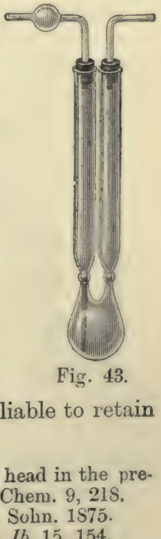

Fig. 43.

I must add that if sulphuric acid is used in absorbing the water generated by the combustion, it must also be used for drying the oxygen and air passed into the combustion tube, otherwise a small error will be introduced.** Hlasiwetz's †† opinion, that sulphuric acid is liable to retain carbonic acid, is unfounded.‡‡

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* The methods of directly estimating oxygen, given under this head in the previous edition, are now discussed in § 192.

† Zeitschr. f. anal. Chem. 9, 218.

‡ Elementaranal. durch Quecksilberoxyd. Berlin, Mittler u. Sohn. 1875.

§ Zeitschr. f. anal. Chem. 4, 177.

|| Compare Dibbits, *Ib.* 15, 154.

¶ Zeitschr. f. anal. Chem. 8, 199.

** Compare the author's experiments, *loc. cit.*, 182; also Dibbits, *loc. cit.*, 145.

†† Chem. Centralbl. 1856, 517.

‡‡ Compare the author's experiments, *loc. cit.*, 183

Tubes filled with anhydrous phosphoric acid are also well adapted for absorbing water, and have been strongly recommended by A. MITSCHERLICH for that purpose (*loc. cit.*). He gives the tube the form shown in fig. 44. It has a bore of 15 mm. and a length of 200 mm. The acid is confined between asbestos plugs placed at each end, and must be quite free from admixed phosphorus. If in any analysis a notable quantity of water has been taken up, and there is any possibility of chlorine, hydrochloric acid, carbonic acid, &c., having been absorbed, it is necessary to expel them, by heating the tube finally so strongly that a moist filter paper hisses when applied to it. As mentioned above, the wide end of the phosphoric acid tube is fixed on to the drawn-out combustion tube by a ring of flexible tube.

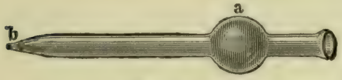

Fig. 44.

3. *As to the absorption of carbonic acid.*

a. Many alterations have been suggested in LIEBIG's potash bulbs. GEISSLER's potash bulbs (fig. 45) stand without support, the gas passes thrice through the potash, and ejection of the latter is almost impossible. The filling or emptying of the apparatus is very simple. As regards the former, *a* is dipped into the potash, and suction is applied at *b*; to empty them, the apparatus is inverted and the operator blows into *a*. One objection to this apparatus is, that the potash in the three bulbs does not communicate; bicarbonate is therefore liable to form in the first bulb, and stop the tube. For this reason GEISSLER's bulbs require fresh filling much more frequently than LIEBIG's * (J. LÖWE †).

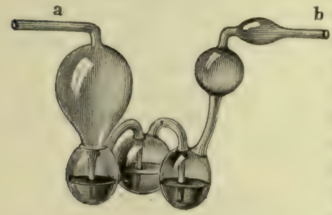

Fig. 45.

Fig. 46 represents E. MITSCHERLICH's bulbs, with a slight modification made by A. MITSCHERLICH. *a b* contains lumps of caustic potash, *b c* anhydrous phosphoric acid, isolated by asbestos plugs at *b* and *c*; a small tube is fixed into *c* by means of a ring of flexible tube, *d*. The apparatus is then filled with solution of potash to such an extent that when in use, and in a slanting position, the passing gases will send some solution into the top bulb.

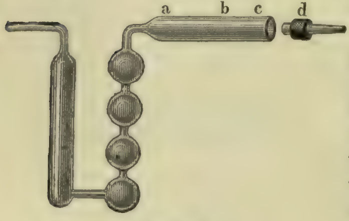

Fig. 46.

DE KONINCK‡ suggests that the tubes joining the bulbs in E. MITSCHERLICH's apparatus should be bent, and enter the bulbs laterally.

b. G. J. MULDER§ has replaced the potash bulbs by a totally different absorption apparatus, in which soda-lime is used instead of solution of potash. According to his original directions, the chloride of calcium tube is immediately connected with the U-tube *a* (fig. 47), containing small pieces of glass, 6 to 10 drops of sulphuric acid, and asbestos plugs at the top: $\frac{7}{8}$ of *b* is filled with granulated soda-lime (about 20 grm.), the remaining $\frac{1}{8}$ in the upper part of the second limb contains chloride of calcium (about 3 grm.): lastly, *c* is filled with lumps of hydrate of potassa. *a* and *b* are weighed together, *c* serves as a guard to *b*, and is not weighed. The sulphuric acid tube serves to show the rate of the evolution of gas, and should contain enough acid to close the lower part of the tube. If the process goes on properly, the weight of this tube does not increase more than 1 mgrm., and very often the increment is unweighable; and if the tube after use is closed with caoutchouc caps, it may be used over and over again. Sulphuric acid has the advantage over other fluids that it indicates whether the combustion is perfect or not; for in the first case it remains colourless, but in the second it becomes brown from the escaping hydrocarbons, and absolutely accurate results cannot be expected. From the author's experiments, it would appear that the increase in the sulphuric acid tube is due to the fact that air dried by chloride of calcium will still yield a trace of moisture to sulphuric acid.

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* NOTE.—The editor has worked for many years with these bulbs, using potash solution sp. gr. 1·27, but has never experienced this inconvenience.

† Zeitschr. f. anal. Chem. 7, 224. ‡ *Ib.* 9, 481. § *Ib.* 1, 2.

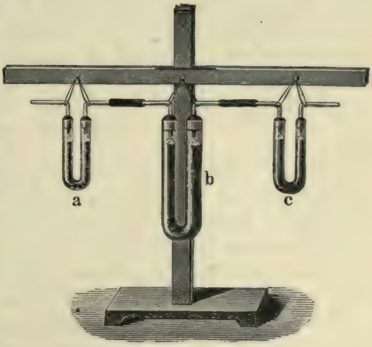

Fig. 47.

The sulphuric acid tube may very well be dispensed with, and all the advantages it offers may be attained by using Schrötter's sulphuric acid tube, fig. 43, p. 33, for absorbing the water.

The absorption of the carbonic acid by the soda-lime tube is as rapid as it is complete; even when a stream of carbonic acid is passing with ten times the rapidity usual in organic analysis, no trace of the acid makes its escape. As the carbonic acid is absorbed, the soda-lime becomes warm; if any water evaporates from the latter, it is retained by the chloride of calcium in the second limb. The corks of the absorption tubes are, like the others, coated with sealing-wax. A filled soda-lime tube weighs about 40 grm. The first time it is used alone; the second time the same tube is used, but as a precautionary measure a second similarly filled tube is placed in front of it and weighed separately. The second tube rarely increases in weight, and, unless it does, the first tube can be used a third time, but of course in connection with the second. If the second tube has gained in the third operation, the first tube is rejected at the fourth operation, and the second is now used alone, &c. If a current of oxygen is passed through the combustion tube after the combustion, the tubes of course become filled with oxygen. If therefore care be taken that the tubes are weighed full of oxygen before the commencement of the experiment, there is no need to pass a current of air through the apparatus at the end of the combustion. For weighing, Mulder closes the ends of the glass tubes with cups made of india-rubber tube. Dibbits,* however, says this is not advisable.

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* Zeitschr. f. anal. Chem. 15, 157.

Mulder's absorption apparatus is peculiarly suitable when the carbonic acid is mixed with another gas. It insures complete absorption, precludes the evaporation of any water, and offers perfect security in case of a sudden and rapid evolution of gas. If it is wished to proceed strictly in accordance with theory, when a sulphuric acid tube is used for the absorption of water, a small sulphuric acid tube should be joined to the front of the soda-lime tube, and weighed with it, to remove any trace of moisture that may not be absorbed by the chloride of calcium. Hydrate of baryta is also an excellent absorbent for carbonic acid, and may be used instead of soda-lime (Kreusler*).

B. ANALYSIS OF COMPOUNDS CONSISTING OF CARBON, HYDROGEN, OXYGEN, AND NITROGEN.

The principle of the analysis of such compounds is in general this: in *one portion*, the carbon and the hydrogen are determined as carbonic acid and water respectively; in *another portion*, the nitrogen is determined in the gaseous form, or is estimated as ammonium platinochloride or from the platinum therein contained, or by neutralizing the ammonia formed from the nitrogen; the oxygen is calculated from the loss.

As the presence of nitrogen exercises a certain influence on the estimation of carbon and hydrogen, we have here to consider not only the method of determining the nitrogen, but also the modifications in the usual method of determining the carbon and hydrogen rendered necessary by the presence of nitrogen.

a. DETERMINATION OF THE CARBON AND HYDROGEN IN NITROGENOUS SUBSTANCES.

§ 183.

1. When nitrogenous substances are ignited with oxide of copper or with chromate of lead, a portion of the nitrogen escapes as gas along with the carbonic acid and aqueous vapor; whilst another very small portion—but which in bodies containing much oxygen is not by any means insignificant—is converted into nitric oxide; and this is subsequently transformed either wholly or partly into nitrous or hyponitric acid by the air in the apparatus. The employment of the methods described in §§ 174, &c., without modification for the analysis of nitrogenous substances, would accordingly give too much carbon, as the potash bulbs would retain not only the carbonic acid, but also the nitrous acid formed, and a portion of the nitric oxide (which in the presence of potash slowly decomposes into nitrous acid and nitrous oxide). This defect may be avoided, on the one hand, by the exclusive use of oxide of copper as oxidizing agent, by a very intimate mixing of the substance with the oxide, and by burning very slowly; and, on the other hand, by selecting a combustion tube about 12—15 cm. longer than those usually employed, filling this in the ordinary way, but finishing with a loose layer, about 9—12 cm. long, of clean fine copper turnings, or a spiral of copper wire or roll of copper foil (§ 66, 5, vol. I.). The copper spiral, &c., cannot be replaced by copper oxide reduced by hydrogen, as this obstinately retains hydrogen, and consequently decomposes a notable portion of the carbonic acid into carbonic oxide and water.†

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* Zeitschr. f. anal. Chem. 5, 216.

† Schrötter, Lautemann: Journ. f. prakt. Chem. 77, 316.

The process is commenced by heating the part of the tube containing the metallic copper to bright redness, and maintaining it in that state during the whole operation. In all other respects the operation is conducted as in the methods above described. The action of the copper depends on its property of decomposing, when in a state of intense ignition, all the oxides of nitrogen into oxygen, with which it combines, and pure nitrogen gas. As the metal has this action only when intensely ignited and when the current of gas is slow, care must be taken to maintain the fore part of the tube at a bright red heat, and not to allow the combustion to go on too rapidly.* As recently reduced metallic copper retains hydrogen, and, when kept for some time, aqueous vapor condensed on the surface, it must be introduced into the tube hot as it comes from the drying closet (which is heated to 100°). LIEBIG recommends that the turnings should be compressed in a tube to a cylindrical form, so as to facilitate their rapid introduction into the combustion tube: spirals of copper gauze, however, are more convenient.

2. If nitrogenous bodies are to be burned in the apparatus described in §178, *a*, the combustion tube should be about 80 cm. long, and the fore part of it filled for a length of 15—18 cm. with clean copper turnings, or with a spiral of copper gauze. Care must be taken that at least the foremost half of the copper remains unoxidized both during the ignition in the current of air and during the actual process of combustion. When the operation is ended, and the oxidation of the metallic copper is visibly progressing, the oxygen is turned off, and the cock of the air gasometer opened a little instead, so that the tube may cool in a slow stream of air.

3. As the metallic copper is oxidized after almost every analysis, and must be again reduced, STEIN† uses silver instead (shreds of the finest silver lace); this has the additional advantage of retaining chlorine. According to CALBERLA's experiments, silver at a bright red heat reduces nitric oxide completely, but has no action whatever on carbonic acid.

b. DETERMINATION OF THE NITROGEN IN ORGANIC COMPOUNDS.

As already indicated, two essentially different methods are in use for determining the nitrogen in organic compounds: in the one the nitrogen is separated in the gaseous state and its volume measured; in the other it is converted into ammonia, and this is estimated either as platinochloride of ammonium or from the platinum in it, or by neutralization.

a. Determination of the Nitrogen by Volume.

The many methods that have been recommended for this purpose may all be arranged under two general heads: the object in one case being the collection of the whole of the nitrogen contained in a weighed portion of the substance; in the other, the determination of the relative proportion merely between the carbonic acid and the nitrogen gas evolved, and from this the quantity of nitrogen is then calculated; it is evident, therefore, that these latter methods require that the amount of carbon contained in the substance should be previously known. The methods based on the former principle are denominated *absolute* or *quantitative*, those based on the latter are called *relative* or *qualitative*. In each class those have been selected which are most readily performed and which give the most accurate results.

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* Compare THORP, J. Chem. Soc. 1866, vol. 19, 359.

† Zeitschr. f. anal. Chem. 8. 83.

1. RELATIVE DETERMINATION OF NITROGEN BY VOLUME.

§ 184.

aa. LIEBIG'S METHOD.*

The method can only be used when the amount of nitrogen in the substance is not too small in proportion to that of the carbon. See also below. The process requires 6 or 8 accurately graduated tubes of strong glass, each about 30 cm. long and 15 mm. in diameter; also a tall cylinder of strong glass, widened at the top (see fig. 49).

The combustion tube should be 60 cm. long and sealed behind: oxide of copper sufficient to form a layer of 6 cm. in length is first introduced into the farther end; about ·5 gram † of the very finely pulverized substance is then most intimately mixed with a portion of the oxide of copper sufficient to fill the combustion tube about half. This mixture is introduced into the tube and followed by another layer of oxide of copper, the rest of the tube—a part at least 12 cm. long—being then filled with copper turnings or a spiral of copper gauze (§ 66, 5, vol. I.). The combustion tube so prepared is connected with the delivery tube, and placed in the furnace; the fore part of the tube is then heated to bright redness, and kept at that temperature throughout the experiment, whilst the part occupied by the mixture is protected by a screen which is shifted back 3 cm. each time as the application of heat is gradually advanced in the usual way. When about one-fourth of the mixture is decomposed, and the atmospheric air is thus almost completely expelled from the tube by the products of combustion, one of the graduated tubes, filled with mercury,‡ is inverted over the mouth of the bent delivery tube, which opens under mercury, and is about three-fourths filled with the gas; it is then lifted out of the mercurial trough, so that the rest of the mercury flows out; if there is not the slightest red coloration of the gaseous contents on looking through the tube lengthwise, the gases are certainly not mixed with nitric oxide. (In order to be absolutely certain that there is no nitric oxide in any of the tubes, this must be repeated at the middle and end of the operation.) After this preliminary experiment, the graduated tubes are filled one after another (see fig. 48), whilst the heating is continued slowly and

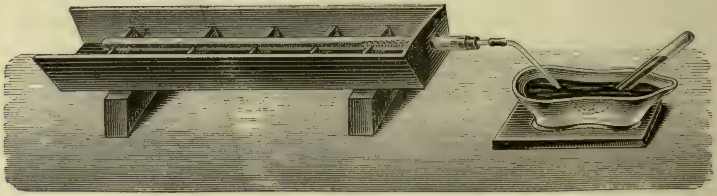

Fig. 48.

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* LIEBIG'S Handbook of Organic Analysis, edited by A. W. HOFMANN, p. 61.

† The weight need not be more accurately known in this process.

‡ The best way of filling a tube completely with mercury, so as to prevent any air-bubbles remaining in it, is to pour in the mercury through a funnel tube reaching down to the bottom of the graduated tube, then close the aperture with the finger, invert the tube, and make the minute bubbles of air adhering to the sides gradually unite with the large bubble at the top. The tube is then turned upright, and completely filled up with mercury.

uniformly. This operation requires a stand with places for six or eight tubes,* or an assistant must hold the filled tubes until they are required for measuring. Care must be taken to mark the order in which they were filled.

When all the tubes are filled, the gaseous mixture in them is determined in the following manner, taking one tube after another:—The tube is completely immersed for some time in the mercury with which the cylinder (fig. 49) is filled, so that the temperature may be uniform and the same as that of the mercury; it is then raised until the mercury on the inside and outside is exactly at the same level, and the volume is read off and noted (see § 13, vol. I.). By cautiously blowing into the pipette, fig. 50, which is nearly filled with potash solution, a small quantity of the liquid is made to pass into the tube. The pipette is then withdrawn, and the absorption of the carbonic acid promoted by moving the tube up and down in the mercury, holding it firmly, and pressing its mouth firmly against the side of the cylinder; finally the tube is once more completely immersed, raised again until the mercury is exactly level inside and outside, and the volume is then read off. (The pressure caused by the small column of potash solution may be altogether disregarded.) The volume of the carbonic acid is determined by subtracting the quantity found in the second measuring (the nitrogen gas) from that noted in the first (nitrogen gas + carbonic acid gas). When the contents of one tube have thus been determined, the mercury is cleaned by washing it first with water slightly acidulated with hydrochloric acid, then with pure water, and drying with blotting-paper; the contents of the next tube are then determined in the same manner.

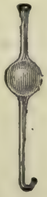

Fig. 50.

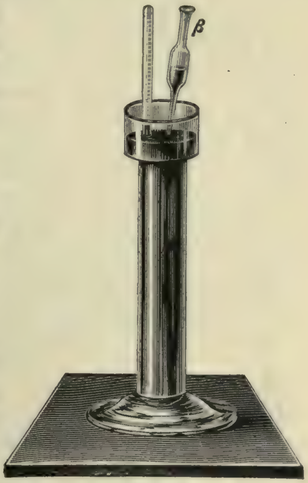

Fig. 49.

The results obtained from the different tubes are generally found to be tolerably uniform; in many cases, however, where the nitrogenous substance, previous to complete combustion, yields decomposition products of different degrees of volatility, there are notable differences in the results obtained from the several tubes. As a general rule, the mean is taken as correct, and this may be considered the more accurate and trustworthy the more closely the results from the individual tubes agree. If, however, the tubes first filled give a considerably larger proportion of nitrogen than those filled subsequently, it may be safely assumed that the air was not completely expelled when the first tubes were filled; in such a case these are not taken into account.

The relative proportion of the carbonic acid to the nitrogen gas expresses directly, and without further calculation, the proportion which the equivalents of the carbon bear to those of the nitrogen: since 1 eq.

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* A stand of this kind will be found described and figured in Das chemische Laboratorium zu Giessen, von J. P. HOFMANN, Heidelberg, 1842.

carbon combines with 2 eq. oxygen, leaving the volume of the latter element unaltered, and giving accordingly 2 volumes of carbonic acid; —and 1 eq. nitrogen likewise gives 2 volumes of nitrogen gas.

Suppose the proportion which the carbonic acid bears to the nitrogen gas to be 4 : 1, the analysed compound will contain 1 eq. nitrogen = 14·04 to 4 eq. carbon = 4 × 6 = 24. If, therefore, we have found 26 parts of carbon in 100 parts of the analysed substance, the latter contains 15·21 parts of nitrogen; since $24 : 14{\cdot}04 :: 26 : x ; \therefore x = 15{\cdot}21$.

There is an unavoidable source of error inherent in this method, as it is impossible to remove the air completely from the tube; the nitrogen therefore is always somewhat too high. Notwithstanding this defect, however, the method leaves no doubt as to the correct ratio, if the amount of nitrogen is considerable; thus, for instance, if the proportion found is 1 : 4·1, it is at once evident that 1 : 4 is the actual proportion. If, however, the relative quantity of the nitrogen is small, this defect vitiates the results; and experience has proved that the method is not suitable for the analysis of substances containing less than 1 eq. nitrogen to 8 eq. carbon.

bb. BUNSEN'S METHOD.*

The method gives more accurate results, but requires more time and trouble, and demands greater skill, than *aa.*

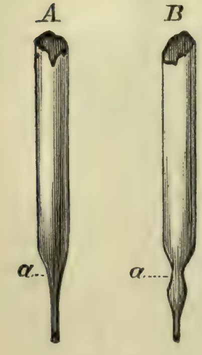

Fig. 51.

In the first place, a tube of strong, difficultly fusible glass, about 38 cm. long and 2 cm. wide, is drawn out at one end, as shown in fig. 51, *A*, then narrowed at the part marked *a*, as shown in fig. 51, *B*. This latter manipulation is necessary to enable the tube to withstand the internal pressure exerted by the gas evolved during ignition. The drawn-out part must, moreover, be particularly stout.

When the tube has been thoroughly cleaned, an intimate mixture of about 5 grams of loose ignited oxide of copper with 3—5 cgrm. of the substance (which, however, need not be accurately weighed) is introduced into it, together with a small quantity of clean copper turnings (§ 66, 5, vol. I.). The other end is then drawn out at a distance of 17—20 cm. from the narrowed part, in the same way as above. Volatile liquid bodies are introduced into the tube, best in a capillary tube sealed at one or both ends.

The tube, as shown in fig. 52, is now connected at one end with a globe, *B*, half filled with sulphuric acid, in which the hydrogen gas evolved from *A* is dried, at the other end with an air-pump, with the cock, *p*, open, to let the hydrogen gas escape.

When the hydrogen has passed through the apparatus long enough to completely expel the air, the cock *p* is turned off, *A* is opened, and *c* compressed by a clamp; the piston of the exhausting syringe is then drawn up with a quick motion, and the cock *s* immediately turned off. This serves to rarefy the hydrogen gas in the tube, and the latter may now be fused off at *d*, in the blowpipe flame, without risk of swelling. Exhaust as completely as possible, and then fuse off the tube also at *b*.

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* See KOLBE's paper on the subject in the Handwörterbuch der Chemie, Supplemente zur ersten Auflage, S. 200.

As the tube prepared in this way would inevitably blow out from the pressure of the evolved gases if it were exposed to a red heat in the usual way, it is necessary to enclose it in a mould made of strong sheet iron (fig. 53).

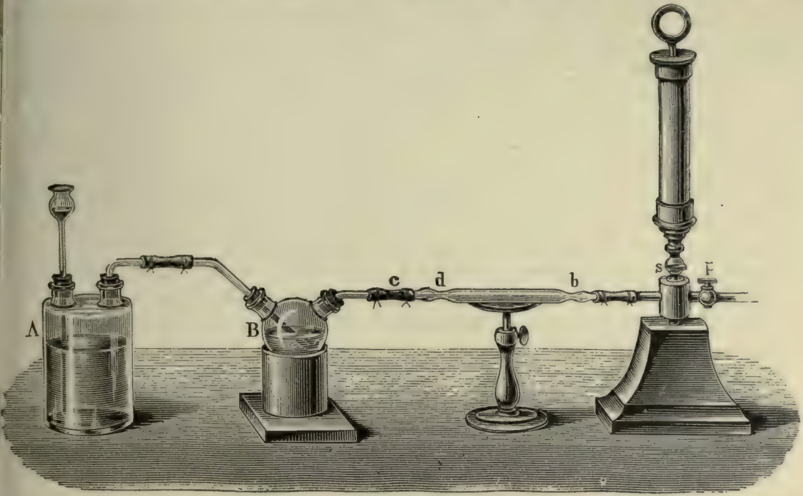

Fig. 52.

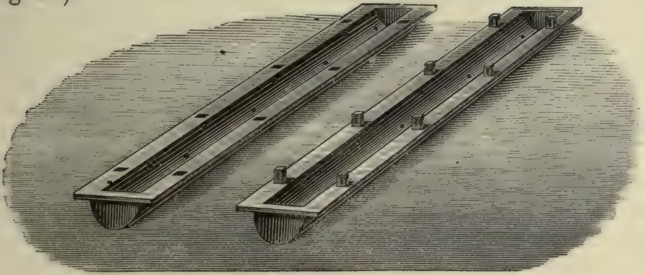

Fig. 53.

The two parts accurately fit each other, inclosing a cylindrical cavity, 30 cm. long and 5—6 cm. in diameter. They are both filled with a paste of freshly prepared plaster of Paris, mixed with a handful of cow-hair cut small; the combustion tube is pressed into the one half, in the middle, and as soon as the paste begins to set, the other half is pressed down upon it, and the mould closed by small iron wedges (see fig. 54).

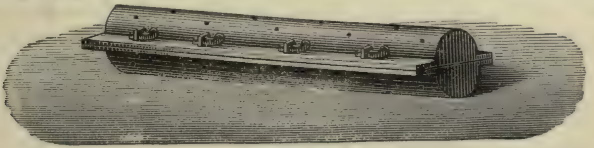

Fig. 54.

There are 10 or 12 holes in the curved part of each half to give free vent to the aqueous vapours, &c.

When the plaster has thoroughly set, the mould is slowly heated to dull redness in a suitable furnace. As soon as the smell of burnt hair diminishes, and the mould, entirely surrounded with red-hot charcoal, is at a bright red heat, the coals are covered with ashes, and the heating continued in this way for another half-hour. When cold, the tube is carefully taken out of the mould; it should look dull and opaque, and have a blistered surface, showing that it has been thoroughly softened in the process. If too large a quantity of substance be used, or if the temperature be too high, the tube will often be blown out in some part. The point is broken off under mercury, so as to receive the gaseous contents in a graduated tube filled with mercury (§ 12, vol. I.), into which a drop of water has been introduced (§ 16, vol. I.); this serves to saturate the moist gas with aqueous vapor. Although it is not necessary to transfer the whole of the gas from the combustion tube to the graduated tube, yet it is advisable to have as large a volume of gas as possible for the subsequent analyses.

The state of the barometer and thermometer, and the height of the mercurial column in the graduated tube, are first noted; a moistened ball of hydrate of potash, fused on to an iron or platinum wire, is then introduced to absorb the carbonic acid gas. When the residual nitrogen gas has been dried, by the introduction of a second unmoistened ball of hydrate of potash, it is measured. The volumes are reduced to the same temperature and pressure, and to the state of dryness; this gives the relative proportion of the volumes of the carbonic acid and nitrogen, and accordingly also that of the equivalents of the carbon and nitrogen in the substance analysed.

cc. MARCHAND'S METHOD,* MODIFIED BY GOTTLIEB.†

The farther end of a long combustion tube is drawn out to an open point; an asbestos plug is introduced, then the mixture of ·1—·12 gram of the substance with a large quantity of oxide of copper, then 6 cm. of pure oxide of copper, a layer of copper turnings, 12—14 cm. long, and lastly 6 cm. of coarsely powdered fused chloride of calcium. The fore part of the tube is now connected with a delivery tube bent at a right angle, the descending limb of which is 80 cm. long, and a current of dried hydrogen is passed for two hours through the apparatus by the drawn-out point; towards the end of the operation the delivery tube must dip under the mercury in the trough. The tube is now sealed at the farther end, the pure oxide of copper is heated (the oxygen of which will combine with the hydrogen, thus creating a vacuum), a graduated tube filled with mercury is inverted over the end of the delivery tube, and the combustion proceeded with. The process will give 90—100 c. c. of gas, of which about half may be used for analysis, the remainder to test for nitric oxide gas. GOTTLIEB obtained very satisfactory results by this method.‡

dd. SIMPSON|| burns the substance with a mixture of oxide of copper and oxide of mercury. For particulars see the original memoir.

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* Journ. f. prakt. Chem. 41, 177.

† Annal. d. Chem. u. Pharm. 78, 241.

‡ HEINTZ'S absolute method of determining nitrogen is founded on the same principle (Journ. f. prakt. Chem. 55, 229).

|| Annal. d. Chem. u. Pharm. 95, 64.

UNIVERSITY

2. Absolute Determination of Nitrogen by Volume.

§ 185.

aa. Dumas' Method.

This method may be used in the analysis of all organic compounds containing nitrogen. A graduated glass cylinder of about 200 c. c. capacity is required, with a ground-glass plate to cover it.

The combustion tube should be about 70 or 80 cm. long, and sealed at the farther end by fusion, like a test-tube. A layer of pure dry bicarbonate of soda, 12—15 cm. long, is first introduced, then a layer of oxide of copper, 4 cm. long; after this an intimate mixture of the weighed substance (·3—·6 gram, or, in the case of compounds poor in nitrogen, a somewhat larger quantity) with oxide of copper, then the oxide which has served to rinse the mortar, followed by a layer of pure oxide, and lastly, a layer of copper in the form of a spiral of wire, a roll of thin foil, or turnings, about 15 cm. long.* When a channel has been made along the top of the tube by gentle tapping, it is connected with the bent delivery tube *c f* (fig. 55), and placed in the furnace; the farther end of the tube (to the extent of about 6 cm.) is gradually heated, protecting the other parts by a screen. The bicarbonate of soda is decomposed by the heat, and the carbonic acid evolved drives the air before it, and expels it from the tube. When the evolution of gas has proceeded for some time, the end of the bent delivery tube is dipped under the mercury, a test tube filled with potash solution inverted over it, and the heat advanced a little towards the fore part of the tube. If the gas-bubbles are completely absorbed by the potash solution, this is a proof that the air is entirely expelled from the tube, and the actual combustion may be at once commenced; if they are not, the evolution of carbonic acid must be continued until the desired point is attained. The graduated cylinder, filled $\frac{2}{3}$ with mercury, $\frac{1}{3}$ with concentrated

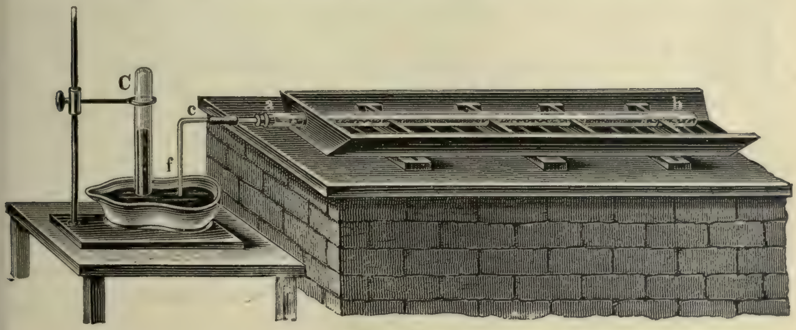

Fig. 55.

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* Melsens (Annal. d. Chem. u. Pharm. 60, 115) recommends tubes of a length of 1·10 to 1·25 mètre, which he fills as follows:—Bicarbonate of soda, 10 cm.; coarse oxide of copper, 20 cm.; the substance, triturated with fine oxide, then mixed with coarser oxide of copper, 30 cm.; coarse oxide, 30 cm.; metallic copper, 20 cm. Stromeyer recommends mixing the oxide of copper with carbonate of soda, in order to prevent the formation of oxides of nitrogen from the first (Annal. d. Chem. u. Pharm. 117, 250).

potash solution, is then inverted over the end of the delivery tube in the mercurial trough, with the aid of the ground-glass plate,* and the combustion proceeded with in the usual way, heating first the fore part of the tube to redness, and advancing gradually towards the farther end. Finally, the other half of the bicarbonate of soda is decomposed, and thus the whole of the nitrogen which still remains in the tube is driven into the cylinder. When the volume of the gas in the cylinder no longer decreases, even on shaking the latter (that is, when the whole of the carbonic acid has been absorbed), the cylinder is placed in a large and deep glass vessel filled with water, the transport from the mercurial trough to this vessel being effected by means of a porcelain dish filled with mercury, or preferably an iron cap with iron strips rivetted on (fig. 56).† The mercury and the potash solution sink to the bottom, and are replaced by the water. The cylinder is completely immersed, then raised again until the water inside and out is at the same level; the volume of the gas is read off, and the temperature of the water and the state of the barometer noted; the weight of the nitrogen is calculated from its volume, after reduction to the normal temperature and pressure, and with due regard to the tension of the aqueous vapor (comp. § 198).‡ The results are generally somewhat too high, about ·2—·5 per cent.; this is owing to the facts that even when carbonic acid is passed for a long time through the tube it fails to expel every trace of atmospheric air adhering to the oxide of copper, and that the nitrogen often contains nitric oxide in small quantity (see next page).

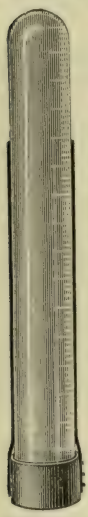
Fig. 56.

It is very advisable, before making nitrogen determinations by this method, to subject a non-nitrogenous substance, such as sugar, to analysis, using the same materials. In this way the analyst learns approximately the extent of the error to which he will be exposed. In such an experiment, the quantity of unabsorbed gas should not exceed 1 or 1½ c. c.

To insure complete combustion of difficultly combustible bodies Strecker § recommends the addition of arsenious acid in powder to the oxide of copper with which the substance is to be mixed; the arsenious acid is volatilized by the action of the heat, the fumes burning the whole of the carbon like a current of oxygen. The arsenious acid sublimes in the fore part of the tube, arsenic remains in the copper.

A variety of modifications of this process have been proposed.

Thudichum and Wanklyn || recommend an intimate mixture of 5

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* The following is the best way of filling the cylinder and inverting it over the opening of the bent delivery tube:—The mercury is introduced first, and the air-bubbles which adhere to the walls of the vessel are removed in the usual way. The potash solution is then poured in, leaving the top of the cylinder free to the extent of about 5 mm.; this is cautiously filled up to the brim with pure water, and the ground-glass plate slided over it. The cylinder is now inverted, and the opening placed under the mercury in the trough; the glass plate is then withdrawn from under the cylinder. In this manner the operation may be performed easily, and without soiling the fingers with the potash solution.

† Reichardt, Zeitschr. f. anal. Chem. 5, 67.

‡ J. T. Brown has given tables for simplifying the calculation (Journ. Chem. Soc. 1865, vol. 18, 211).

§ Handwörterbuch der Chemie, 2. Aufl. 1, 878.

|| Journ. Chem. Soc. 1869, vol. 22, 293.

parts anhydrous carbonate of soda, and 13 parts fused dichromate of potassa for evolving carbonic acid: it has the advantage of containing no water. They also consider it necessary to adopt FRANKLAND's * proposal, and determine the nitric oxide which is generally present in small quantity in the nitrogen. This is done, after reading off the volume of the gas, by adding a small quantity of oxygen, removing the excess not used up in oxidizing the nitric oxide by pyrogallic acid, and then reading off again. The difference is the nitric oxide, the residue pure nitrogen. 1 vol. nitric oxide contains ½ vol. nitrogen. Finally, they prefer to measure the gas over mercury, instead of water, which causes minute errors from its contained air.

L. KESSLER † advises the collection of the gases in an india-rubber bag free from sulphur, and containing some potash solution, and then transferring them to the graduated tube.

Instead of evolving the carbonic acid within the tube, it may be generated in a separate apparatus. The combustion tube is connected behind with a mercurial valve (fig. 36, p. 27), and this again with the apparatus by means of a tube, which can be closed by a glass stopcock or a clip. The apparatus must allow the escape of the carbonic acid when the cock is closed, and must deliver the gas at a tension which will readily overcome the pressure of the mercury at the other end.

bb. SIMPSON'S METHOD.‡

The *principle* of this method, which is well suited for the analysis of all nitrogenous bodies, and gives accurate results also in the case of difficultly combustible organic compounds, is the same as that of DUMAS' method (*aa*); but the *process* differs in some essential points. The carbonic acid which serves to expel the air from the tube is evolved from manganous carbonate; the combustion is effected by a mixture of oxide of mercury with oxide of copper; the free oxygen gas is absorbed by copper in a state of ignition; the gaseous mixture is received in a special apparatus, in which the carbonic acid is removed by potash solution, the nitrogen being then transferred to a graduated tube, and finally measured over mercury.

A strong combustion tube is chosen, about 80 cm. long, and one end is sealed in the blowpipe flame. A mixture of 12 grams of manganous carbonate, dried at 100°, with 2 grams oxide of mercury, is then introduced.§ A plug of recently ignited asbestos is inserted, leaving 3 cm. clear space between it and the mixture, so as to admit of the formation of a sufficiently wide free passage for the evolved gas when the tube is placed in a horizontal position; after this 1 gram of oxide of mercury. The accurately weighed substance (about ·5 or ·6 gram) is mixed with 45 times its weight of a previously prepared and dried mixture of 4 parts of recently ignited oxide of copper and 5 parts of oxide of mercury, and the mixture transferred, without loss, to the combustion tube, the mortar rinsed with some pure oxide of copper and some mixture of oxide of copper and oxide of mercury, and the rinsings also transferred to the combustion tube. Another asbestos plug is now inserted, which should be distant about 30 cm. from the first, bearing in mind that a free passage of ample width should be left clear above the mixture when the tube is placed in a horizontal position; and also that the plug is partly intended to clear that part of the tube through which it passes off the particles of the mixture adhering to the sides. A layer of pure oxide of copper, 6—9 cm. long, is now introduced, then a third asbestos plug, and finally a layer, 20—24 cm. long, of metallic copper (prepared by reducing granular oxide of copper in a current of hydrogen at a rather low temperature).* The fore part of the tube is drawn out, and connected, by means of a small caoutchouc tube, with a delivery tube, bent below at a right angle, and dipping into the mercurial trough.

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* Phil. Trans. 147, 62. † Compt. rend. 74, 683; Zeitschr. f. anal. Chem. 11, 445.

‡ Annal. d. Chem. u. Pharm. 95, 74.

§ The oxide of mercury insures the non-formation of carbonic oxide gas, which might otherwise be produced from accidental presence of organic matter.

When a free passage for the evolved gases has been cleared by a few gentle taps, the tube is placed in the combustion furnace, and the apparatus prepared for the reception of the gaseous mixture (fig. 57). This should be strongly made, and hold about 200 c. c.; the upper part being about 7 or 8 mm. in diameter outside. A strong vulcanized india-rubber tube, 5 cm. long, is pushed over the point, leaving about 3 cm. of tubing projecting beyond, and securely tied with silk cord; a solid glass rod, ground at both ends, 15 mm. long, and of the same diameter as the india-rubber tube, is inserted into it and pushed down until it touches the point of the vessel; finally, a very narrow gas-delivery tube of the same diameter as the glass rod is inserted into the upper part of the caoutchouc tube still left free; and tied securely. Then tie silk cord round the portion occupied by the glass rod. This is intended to close the vessel air-tight. To ascertain whether the vessel is really air-tight, it is partly filled with mercury, inverted in the trough, and observed to see if the mercury will fall. If this experiment shows the joints to be perfectly air-tight, the apparatus is filled with mercury and 16 or

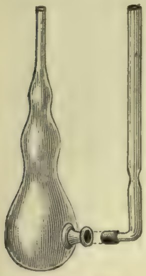

Fig. 57.

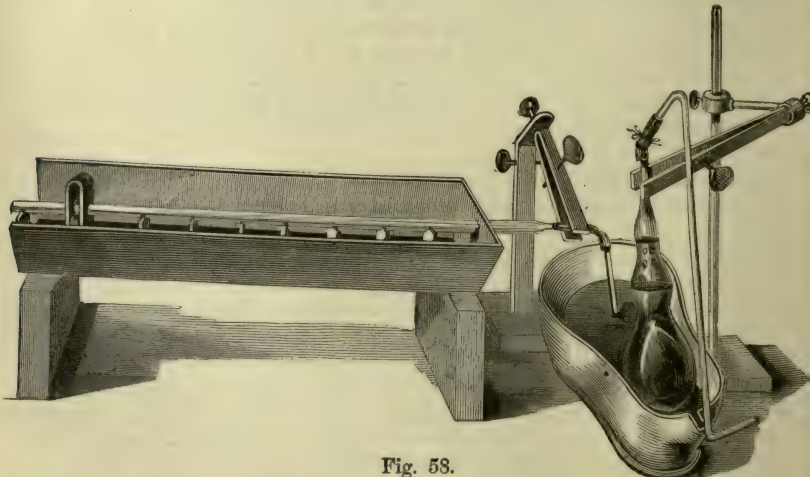

Fig. 58.

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* For the modifications required in the process of filling, when liquids are to be analysed, the original paper (*loc. cit.* p. 83) must be consulted.

17 c. c. of concentrated solution of potassa, replaced in the trough, and secured in the manner shown in fig. 58.

The hindermost half of the layer of manganous carbonate is separated by a screen and heated a few minutes with red-hot charcoal,* until the disengaged carbonic acid has expelled the air from this part of the tube; the charcoal is then removed, and the other half of the manganous carbonate before the screen is gradually heated to redness, as well as the copper and oxide of copper in the fore part of the tube, the portion occupied by the mixture being protected by screens. As soon as the evolution of carbonic acid ceases, the end of the gas delivery tube, which has dipped into the mercury from the commencement, is inserted (without lifting it above the mercury) into the orifice of the gas apparatus; and the mixture itself heated, proceeding slowly from the fore part to the farther end. Both the fore part of the tube and the part occupied by the exhausted portion of the manganous salt must be kept red-hot during the whole process of combustion.

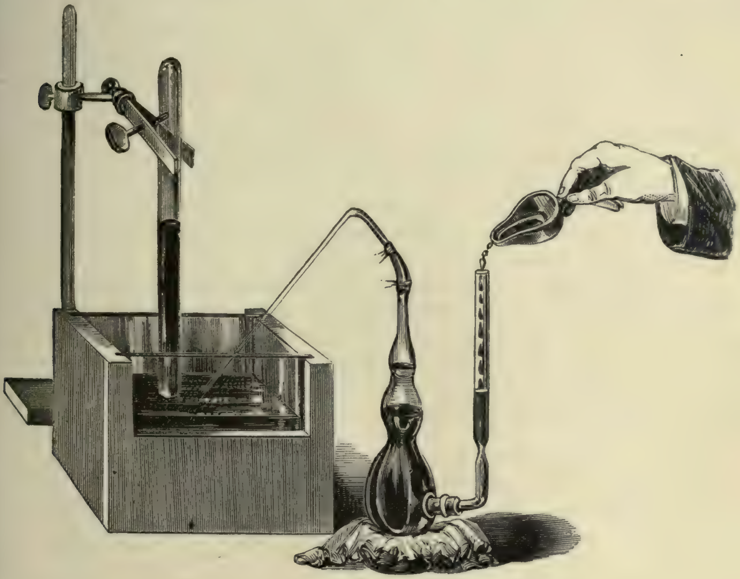

Fig. 59.

When the combustion is at an end, the remainder of the manganous salt behind the screen must be decomposed, and the carbonic acid evolved will drive all the nitrogen into the receiver. As soon as the gas-bubbles are completely absorbed by the potash solution, the gas delivery tube may be removed.

To transfer the nitrogen collected in the apparatus to a graduated tube for measuring, a tube of the form shown in fig. 57 is fitted, under the mercury, into the tubulure of the gas vessel, by means of a perforated cork, taking care to moisten the cork previously with solution of chloride of mercury, so as to guard against the possible introduction of air into the gas vessel. Mercury is now poured into the tube until it reaches a considerably higher level than in the gas vessel, and the whole is allowed to stand for two hours, so that all the carbonic acid may be absorbed.

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* Of course, either a gas or charcoal furnace can be used.

In the meanwhile, the graduated tube for measuring the nitrogen is filled with mercury, after a drop of water has been introduced, and is inverted in the trough.

The point of the delivery tube connected with the gas vessel is now introduced under the opening of the measuring tube, the silk cord round the portion of the caoutchouc tube occupied by the glass rod is untied, and mercury is poured into the upright tube (see fig. 59). When the gas has in this manner been almost completely driven over into the measuring tube, the mercury should be added drop by drop, until the potash solution just begins to make its appearance in the gas delivery tube. In this way, exactly as much nitrogen is kept out of the measuring tube as air had at first entered (from the delivery tube). Care must be taken, in pouring in the mercury, that no air is carried with it; for this purpose, the upright tube should from the first be kept tolerably full, and the glass rod in the caoutchouc tube be selected of such a thickness as to oppose considerable resistance to the passage of the gas.

The state of the barometer and thermometer is noted, the moist gas measured, and the weight calculated from the volume. SIMPSON obtained very satisfactory results by this method, in the analysis of alkaloïds, nitrate of potassa, and chloride of ammonium.

It would be advisable, however, before calculating the nitrogen, to test it for oxygen and nitric oxide.

cc. W. GIBBS'S METHOD.

FRANKLAND and ARMSTRONG'S* method of water analysis includes a process for estimating nitrogen, which depends on the exhaustion of the combustion tube by a SPRENGEL pump before and after the combustion.

W. GIBBS† has since published a process in which also the SPRENGEL pump is used. This is in general a combination of FRANKLAND and ARMSTRONG'S method with SIMPSON'S, but differs from these in many respects. It gave excellent results in the analysis of asparagine and allantoin. Reference must be made to the original paper for the construction of GIBBS'S pump, which is less fragile than that used by FRANKLAND and ARMSTRONG. The operation is conducted as follows:—

The rather short combustion tube is filled first with a few grams of carbonate of magnesia, and then with a mixture of the substance with chromate of lead and 5 or 6 grams of chromate of mercury. The fore part of the tube is charged with freshly reduced and finely divided metallic copper. A glass tube, one end of which is connected with the iron T-piece of the pump, is now fixed into the combustion tube by a caoutchouc stopper. To make sure that the apparatus is tight, set the pump in action for a few minutes, allow to stand some time, and notice whether the height of the mercury remains unchanged. When the combustion tube is fully exhausted, which requires from five to ten minutes, the carbonate of magnesia is cautiously heated until the whole apparatus is full of carbonic acid, and the pressure within and without is equal. The combustion is then carried out in the ordinary way. When it is finished, the pump is again set in action until a complete vacuum is attained. SIMPSON's receiver (fig. 57, p. 46) is used to collect the gas, but filled solely with mercury. Finally, the carbonic acid is absorbed by about 50 c. c. potash solution of 1·2 sp. gr., the nitrogen is transferred to the measuring tube, and the process is completed as in *bb*.

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* Journ. Chem. Soc. 1868, vol. 21, 77.

† Amer. Journ. Sci. and Arts, vol 48; Zeitschr. f. anal. Chem. 11, 206.

β. Determination of Nitrogen by conversion into Ammonia (VARRENTRAPP and WILL).

§ 186.

This method is founded on the same principle as the method of examining organic bodies for nitrogen (§ 172, 1, *a*)—viz., that, when nitrogenous bodies are ignited with an alkaline hydrate, the water of hydration of the latter is decomposed, the oxygen combining with the carbon of the organic body to form carbonic acid, which then unites with the alkali, whilst the hydrogen, at the moment of its liberation, combines with the whole of the nitrogen present to form ammonia.

In the case of substances rich in nitrogen, such as uric acid, mellon, &c., the whole of the nitrogen is not at once converted into ammonia in this process: a portion of it combines with part of the carbon of the organic matter yielding cyanogen, which then unites, either in that form with the alkali metal, or as cyanic acid with the alkali. Direct experiments have proved, however, that even in such cases the whole of the nitrogen is ultimately obtained as ammonia, if the hydrated alkali is present in excess, and the heat continued for a sufficient length of time.

As in all organic nitrogenous compounds the carbon preponderates over the nitrogen, the oxidation of the former at the expense of the water, will invariably liberate a quantity of hydrogen more than sufficient to convert the whole of the nitrogen present into ammonia; for instance,

$$C_2N + 4HO = 2CO_2 + NH_3 + H.$$

The excess of the liberated hydrogen escapes either in the free state, or in combination with the unoxidized carbon, according to the relative proportions of these two elements and the temperature, as marsh gas, olefiant gas, or vapour of readily condensible hydrocarbons, these gases serving to dilute the ammonia to a certain extent. As it is necessary, for the success of the operation, that the ammonia should be diluted, it may be here stated that substances rich in nitrogen should be mixed with more or less of some non-nitrogenous body, such as pure sugar (sugar candy recrystallized from alcohol).

It was formerly supposed that this method was applicable to all nitrogenous substances, except those containing the nitrogen in the form of nitric acid, hyponitric acid, &c. This assumption is now no longer tenable, as careful experiments have shown. Even if some of the charges against the process may be put down to incorrect working and impure soda-lime, especially soda-lime containing nitrate of soda, still in some cases the results obtained cannot be referred to these causes. Thus STRECKER found the results to be too low with guanidine, and KONINCK and MARQUART the same with bryonicine. RITTHAUSEN and KREUSLER* also obtained results much too low with leucine, until the substance was burnt with addition of sugar. An animated discussion has been raised as to whether the method is applicable to albuminoid bodies; thus NOWACK and SEEGEN† deny that it is, whilst KREUSLER‡ considers their results, which differ entirely from his own, to be due to nitrate of soda in the soda-lime: and ABESSER and MÄRCKER,§ in the estimation of nitrogen in gluten, horse-flesh, and blood albumin, obtained results which were ·22 to ·23 and ·33 below the volumetric estimations. On the other hand, E. SCHULZE|| found the method to be applicable to vegetable substances (beet, tobacco) containing nitrates, if the amount of the nitrate does not exceed a certain proportion; thus, with 2 to 3 per cent. nitric acid the results were quite accurate, whilst with 6 to 7 per cent. the nitrogen found was about ·2 per cent. too low.

The ammonia formed in the combustion with soda-lime is determined by receiving it in dilute hydrochloric acid, converting the chloride of ammonium formed into platinochloride of ammonium, which is then either weighed as such, or ignited and weighed as metallic platinum.

Many nitrogenous organic compounds give no ammonia when ignited with soda-lime, but yield other volatile nitrogenous bases free from oxygen: thus indigo yields aniline; narcotine, morphine, quinine, and cinchonine yield new volatile bases. Like ammonia, all these volatile bases have the property of forming platinochlorides with hydrochloric acid and bichloride of platinum. Now, it would be committing a serious blunder to take these double salts for platinochloride of ammonium, weigh them, and calculate the nitrogen from the weight found. By igniting them, and calculating the nitrogen from the residuary metallic platinum, all error is avoided, as these platinochlorides, like that of ammonia, contain 1 eq. nitrogen to each eq. platinum (LIEBIG). No theoretical explanation is required in order to understand the other part of the process (the collection and determination of the ammonia).

aa. Requisites.

1. THE SUBSTANCE.—This must be in the form of finest powder, a condition not always easy to attain, with albuminoid bodies for instance. In many cases, however, it is indispensable in order to obtain good results. H. RITTHAUSEN,¶ who has called particular attention to this detail, gives a method of reducing albuminoid bodies to fine powder. The substance, when dried, is transferred for weighing to a tube, such as shown fig. 2, p. 8, if the mixing with the soda-lime is to be effected in a mortar; but if the mixture is to be made in the combustion tube by a wire, a longer and thinner tube is used (compare § 175).

2. A COMBUSTION TUBE of the kind described § 174, 3, about 40 cm. long and 12 mm. wide. For the furnace to be used see § 174, 16.

3. SODA-LIME.** (See § 66, 4, vol. I.)—The caustic soda used in its preparation should be made by the analyst himself from the crystallized carbonate, as commercial caustic soda nearly always

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* Zeitschr. f. anal. Chem. 10, 350.

† *Ib.* 11, 324; 12, 316; 13, 460. ‡ *Ib.* 12, 354. § *Ib.* 12, 447. || *Ib.* 6, 384.

¶ Journ. f. prak. Chem. N. F. 8, 10; Zeitschr. f. anal. Chem. 13, 240.

** S. W. JOHNSON (Zeitschr. f. anal. Chem. 12, 222 and 446) recommends as a substitute for soda-lime a mixture of 1 vol. dry carbonate or sulphate of soda and 1 vol. dry hydrate of lime.

contains nitrate; the presence of the latter is the source of many errors. The best test to ascertain whether soda-lime is free from nitrogenous matter is to make a combustion with chemically pure sugar. The soda-lime should not fuse, but only cake, even when rather strongly heated; and on evaporating the hydrochloric acid with bichloride of platinum, and treating the residue with spirit of wine, no ammonium platinochloride should remain.

Sufficient of the sandy and granular soda-lime required to fill the tube is moderately heated in a platinum or porcelain dish, so that it may be perfectly dry. In the analysis of non-volatile substances, the best way is to use the soda-lime while still warm.

4. Asbestos.—A small portion of this substance is ignited in a platinum crucible previous to use.

5. A Varrentrapp and Will's Bulb-apparatus.—Fig. 60*a* shows its form. It is filled with hydrochloric acid of 1·07 sp. gr. to the extent indicated in the drawing, either by dipping the point into the acid, and applying suction at *d*, or by means of a pipette.

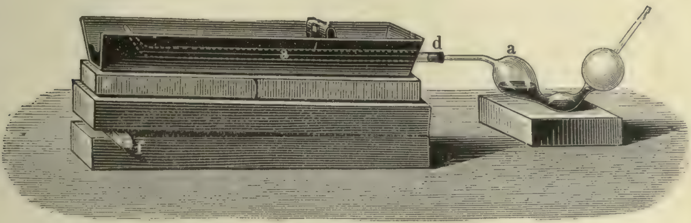

Fig. 60.

In order to guard against the receding of the hydrochloric acid into the combustion tube, Arendt and Knop have suggested the form shown in fig. 61. Péligot's bulbed U-tube, § 187, may also be used.

6. A soft, well-perforated Cork, or India-rubber Stopper, which fits the combustion tube air-tight, and in which the tube *d* of the bulb apparatus fits closely. E. Mulder* advises coating the cork with tinfoil, to prevent it from absorbing ammonia.

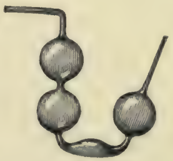

Fig. 61.

7. A Suction Tube filled with hydrate of potassa, and closed at the anterior end with a perforated cork, through which the point of the bulb apparatus passes; or, an aspirator.

8. A Mixing Mortar (§ 174, 8).

9. A sheet of glazed paper.

The reagents, &c., required for the after-treatment of the liquid obtained in the process of combustion are omitted here, as it is not necessary to have them ready at the beginning of the operation.

bb. The process.

The combustion tube is half filled with sandy soda-lime, which is then gradually transferred to the perfectly dry and, if the nature of the substance permits, rather warm mortar, where it is most intimately mixed with the weighed substance (comp. § 174), forcible pressure being carefully avoided; a layer of sandy soda-lime, occupying about 3 cm., is now introduced into the hinder part of the combustion tube, and then the mixture; the latter, which will occupy about 18 cm., is followed by a layer of about 5 cm. of soda-lime which has been used to rinse the mortar, and this again by a layer of 10 cm. of pure (preferably granulated) soda-lime, leaving thus about 4 cm. of the tube clear. The tube is then closed with a loose plug of asbestos, and a free passage for the evolved gases formed by a few gentle taps, after which it is connected with the bulb apparatus by means of the perforated cork or stopper, and finally placed in the combustion furnace (see fig. 60). To ascertain whether the apparatus is air-tight, some air is expelled by holding a piece of red-hot charcoal or a hot tile to the bulb *a*, and the apparatus observed, to see whether the liquid will, upon cooling, permanently assume a higher position in *a* than the other limb. The tube is then gradually heated, commencing at the fore part, and progressing slowly towards the tail, the operation being conducted exactly as in an ordinary combustion (§ 174). Care must be taken to keep the fore part of the tube at a moderate red heat throughout the process. If it is too cool, fluid hydrocarbons will appear in the hydrochloric acid, and cause inconvenience; if it is too hot, ammonia may be decomposed into nitrogen and hydrogen. The stopper or cork should be kept sufficiently hot to guard against its retaining water, and with this, ammonia. The combustion should be conducted so as to maintain a steady and uninterrupted evolution of gas, otherwise the hydrochloric acid is liable to recede; this indeed, is inevitable if the evolution actually ceases for a short period, and may take place with such violence as to force the acid into the combustion tube, which of course spoils the analysis. With compounds very rich in nitrogen, even the greatest care in conducting the process would prove unavailing against the powerful affinity of the hydrochloric acid for the almost pure ammoniacal gas in the tube. This difficulty may be readily met, however, by mixing with the substance an equal quantity of chemically pure sugar (white sugar-candy recrystallized from alcohol*), which will give rise to more permanent gases and dilute the ammonia.

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* Chem. Centralbl. 1861, 44; Zeitschr. f. anal. Chem. 1, 98.

When the tube is ignited throughout its length, and the evolution of gas has just ceased,† the point of the combustion tube is broken off, and air to the extent of several times the volume of the gas in the tube is sucked through the apparatus, to sweep all the rest of the ammonia into the hydrochloric acid; to guard against the inhalation of acid fumes, the suction tube is filled with hydrate of potassa, or a small aspirator is used.‡

If the substance to be analysed contains ammonium salts, a loss of ammonia will be unavoidable if it is mixed with the soda-lime in a mortar. In this case, the mixing must be done in the combustion tube with a wire (§ 175). Many chemists prefer this mode of mixing in ordinary cases as well.*

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* For the nitrogen in commercial sugars see KREUSLER, Zeitschr. f. anal. Chem. 12, 362. White sugar-candy contains about ·012 per cent. nitrogen, fine white refined from colonial sugar ·055, from beet 0·039.

† This takes place when all the carbon deposited on the surface of the mixture is oxidized, as is indicated by the mixture again becoming white.

‡ The suction may be altogether avoided by adopting BOUIS' proposal, and placing a layer of oxalate of lime, dried at 110°, in the hind part of the tube.

Liquid nitrogenous compounds are weighed in small sealed glass bulbs, and the process is conducted as directed in § 180, with this difference, that soda-lime is substituted for oxide of copper. It is advisable to employ tubes of greater length for the combustion of liquids than are required for solid bodies. The best method of performing the operation is to heat first about one-third of the tube at the fore part, which is best filled with granulated soda-lime, and then to force the liquid from the bulbs into the tube by heating the hinder end of the latter; the expelled liquid will thus become diffused in the central part of the tube without being decomposed: a steady and uniform evolution of gas may be easily maintained if the tube is gradually heated from the fore part backwards.

When the combustion is ended, the bulb apparatus is emptied, through the opening at the point, into a small porcelain dish, and rinsed with water until the rinsings no longer have an acid reaction. If liquid hydrocarbons have been formed, the liquid is passed through a moistened filter to separate them. The acid liquid containing the chloride of ammonium is evaporated to a small volume, solution of *pure* bichloride of platinum† is added in excess, and the mixture evaporated to dryness on a water-bath; the residue is treated with a mixture of 2 volumes of strong alcohol and 1 volume of ether. If the liquid acquires a bright yellow colour, this may be taken as a proof that the quantity of bichloride of platinum added was sufficient; if not, a fresh portion (best in alcoholic solution) must be added.‡ The residue of platinochloride of ammonium is finally collected upon a weighed filter which has been dried at 125°, washed with the above-mentioned mixture of alcohol and ether, dried, and weighed (comp. § 99, 2, vol. I.). The dried filter is weighed between two closely fitting watch-glasses held together by a clip. The platinochloride of ammonium thus obtained is not always of a fine yellow colour, but sometimes darker and brownish-yellow. This happens more especially with difficultly combustible substances rich in carbon, as it is less easy in such cases to avoid the formation of liquid hydrocarbons which blacken the hydrochloric acid in the process of evaporation. Direct experiments have proved, moreover, that this coloration does not perceptibly impair the accuracy of the results. The platinochloride may be purified, especially if its quantity is not very large, by dissolving it on the filter with boiling water, collecting the filtrate in a weighed platinum dish or porcelain crucible, and evaporating it together with the washings. After drying it at 125°, the increase in weight of the dish or crucible represents the quantity of pure ammonium platinochloride.

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* Ritthausen, Zeitschr. f. anal. Chem. 13, 240.

† If the bichloride of platinum contains chloride of potassium or chloride of ammonium, the nitrogen found will be too high; if it contains nitric acid, this will cause the formation of chlorine during the evaporation, and a portion of the ammonia will be destroyed, and the nitrogen will be too low. It is therefore always necessary to carefully test the bichloride of platinum before using it.

‡ As the platinochlorides of some of the volatile bases produced in the decomposition of many nitrogenous organic substances (see above) are more readily soluble in alcohol than ammonium platinochloride, ether mixed only with a few drops of alcohol should be used for washing, instead of the ordinary mixture of alcohol and ether, if there is reason to suspect that such double salts are present (A. W. Hofmann).

To test whether the platinochloride is pure, it must always be converted into platinum according to § 99, 2, vol. I. If volatile nitrogenous bases have been formed with the ammonia, the nitrogen can only be estimated from the *metallic platinum* (p. 50).

In the analysis of substances for which the method is especially adapted (see pp. 49 & 50*), and when pure soda-lime is used, the results are accurate, generally rather too low than too high, about 99·5 for 100. This may be owing to traces of chloride of ammonium escaping condensation in the absorption apparatus, and being carried off with the permanent gases;† or to the combustion being incomplete, nitrogenous products of decomposition being evolved which are not precipitated by bichloride of platinum; or, finally, a portion of the ammonia being decomposed into hydrogen and nitrogen. It will be readily seen that, when, with a view of avoiding the second source of error, a longer layer of granulated soda-lime is used (as E. MULDER has proposed), the liability to error from the last source is increased (W. KNOP‡). If the results are too high, this is usually owing to impunity in the bichloride of platinum. Any error arising from this source or from the presence of ammonia in the acid may be guarded against by taking quantities of hydrochloric acid and bichloride of platinum equal to those used in the analysis, and treated in precisely the same way. If any platinochloride is obtained, this small quantity is deducted from the result of the analysis.

Soda-lime containing nitrate or nitrite may either increase or possibly reduce the result, from the combustion of part of the ammonia by the nitrate or nitrite (KREUSLER§).

γ. Péligot's Modification of Varrentrapp and Will's Method.

§ 187.

The essential part of this modification consists in this, that the ammonia generated in the process of combustion with soda-lime is received in a measured quantity of standard sulphuric or oxalic acid; by neutralizing the remaining free acid with standard solution of soda (or baryta water) the amount of the acid saturated by the ammonia, and accordingly also the quantity of ammonia is determined (comp. § 99, 3, vol. I.).

The most convenient way is to use the normal sulphuric or oxalic acid (§ 215). 10 c. c. of this, containing ·49 gram of hydrated sulphuric acid or ·63 of crystallized oxalic acid, and corresponding therefore with ·1704 of ammonia, or ·1404 of nitrogen, will generally suffice for the analysis of ·5 gram of a substance containing 10—20 per cent. of nitrogen. The acid may be placed in the bulbs, fig. 60 or 61. In this case the fluid is accurately measured off into a beaker, as much as possible is sucked up into the bulbs, and the point is rinsed; after the combustion, the acid is emptied into the same beaker, the bulbs are rinsed, and the liquid is then neutralized. The receiver, fig. 62, however, is more suitable for the purpose. The tube *a*—previously provided with the caoutchouc stopper *b*—is first connected by means of a good cork with the combustion tube, and then with the U-tube, which must be ready charged with a little water and the proper quantity of acid from a Mohr's burette. When the combustion is ended and air has been drawn through the apparatus, the tube *a* is rinsed into the apparatus *c*, some tincture of litmus added, and solution of soda run into the tube from a second burette until the acid is almost blue. Now pour the contents of the apparatus into a beaker, rinse with water, and complete the neutralization. With this receiver neither receding nor spirting is much to be feared. By not pouring out the liquid until it is nearly saturated, less water is required for rinsing.

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* LIEBERMANN (Annal. d. Chem. 181, 103), in the analysis of milk, invariably obtained decidedly lower results by this method than by DUMAS'.

† On this account E. MULDER replaces the so-called nitrogen-bulbs by a U-tube containing broken pieces of glass moistened with hydrochloric acid.

‡ Chem. Centralbl. 1860, 44.

§ Zeitschr. f. anal. Chem. 12, 363.

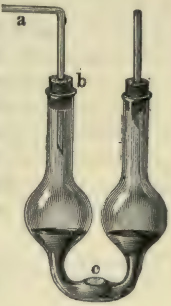

Fig. 62.

Of course the receiver may be varied in form; thus J. Volhard* recommends a modification of Varrentrapp and Will's apparatus, in which the anterior bulb and point are replaced by an Erlenmeyer's flask of 150—200 c. c. capacity.

The standard solution of soda must be quite free from carbonic acid. The author prefers to dilute it so that about 3 c. c. neutralize 1 c. c. acid. Many chemists prefer dilute baryta water instead. In the case of highly coloured liquids, litmus paper should be used instead of the tincture.

Péligot's modification is specially valuable for technical and agricultural purposes. With an experienced operator and correct standard fluids and measuring vessels, it is scarcely less accurate than that described in § 186.

The results obtained by different analysts, however, are not in accord in this respect; thus Märcker† maintains that titration gives lower results than the platinum method with bodies rich in nitrogen and carbon (such as gluten), because aniline-like products are produced which escape the titration; whilst Kreusler,‡ in the analysis of beef, residues of meat extract, and conglutin by the two methods obtained numbers almost identical, and these results agreed, moreover, with those got by Dumas' process.

In using this method in a manufactory, such as manure works, it is worth while to employ an iron instead of a glass combustion tube. To show how this can be done, a process recommended by Thibault is here described.§ He recommends the use of a wrought-iron tube 20 mm. bore and 90 cm. in length. It projects 15 cm. from the furnace at each end. Both orifices are closed by corks fitted with narrow glass tubes. In the fore part of the tube is a layer of granular soda-lime 35 cm. long, kept in its place by iron-wire plugs. The substance is mixed with soda-lime in powder, in a boat of iron plate, 20 cm. long, which is inserted in the tube from behind. The usual apparatus is used to contain the acid. The operation is conducted as follows. The empty combustion tube is first heated to redness in order to purify it, a current of pure hydrogen being passed through it. When cold, the front part is charged with the granular soda-lime, the boat containing powdered soda-lime is inserted from behind, and the tube is heated to redness, whilst a current of hydrogen is passed through. The hinder part is now allowed to cool, the boat is withdrawn by a wire, a little of the soda-lime is taken out, the weighed substance is mixed with the remaining contents of the boat, and the mixture covered with the soda-lime which had been removed. The boat is then reinserted in the tube, and the mixture is gradually heated to redness in a gentle current of hydrogen. When the combustion is ended, and the acid has been removed, the boat is taken out, the tube is heated more strongly, and a more rapid current of hydrogen is passed, in order to free the layer of granulated soda-lime from condensed hydrocarbons. The tube is now ready for the next analysis, and with a number of boats a whole series of analyses may be executed without intermission.

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* Annal. d. Chem. 176, 282; Zeitschr. f. anal. Chem. 14, 332.

† Zeitschr. f. anal. Chem. 12, 221. ‡ *Ib.* 12, 357.

§ J. Pharm. Chem. (4), 22, 39.; Journ. Chem. Soc., 1876, i. 433.

C. ANALYSIS OF ORGANIC COMPOUNDS CONTAINING SULPHUR.

§ 188.

The usual method of determining the carbon in organic bodies by combustion with oxide of copper or chromate of lead would give results too high in the analysis of compounds containing sulphur; since—more especially if oxide of copper is used—a portion of the sulphur would be oxidized to sulphurous acid, and this would be absorbed with the carbonic acid in the potash bulbs. To remedy this defect, LIEBIG and WÖHLER interpose between the chloride of calcium tube and the potash bulbs a tube 10—20 cm. long, filled with perfectly dry binoxide of lead. According to CARIUS'S* experiments, this means is, on the one hand, insufficient to retain all the sulphurous acid produced in the case of substances rich in sulphur, and, on the other, it affects the accuracy of the carbon determination, as peroxide of lead has the power of taking up not inconsiderable quantities of carbonic acid (BUNSEN). CARIUS recommends to burn the substance containing sulphur, in a tube 60—80 cm. long, with chromate of lead, care being taken that the anterior 10—20 cm., which contains pure chromate of lead, is never heated above low redness. The chromate of lead may be used again three or four times without refusion; and, finally, if treated by VOHL'S method (vol. I., p. 107), it is just as fit for use as if it had not been employed for the combustion of a substance containing sulphur.

With regard to CLOËZ'S method of treating the bodies in question, see § 192.

The presence of sulphur demands no modification in the processes described §§ 185, 186, and 187, for the determination of nitrogen. As regards the *estimation of the sulphur* itself, that element is usually weighed in the form of sulphate of baryta, into which it may be converted either in the dry or in the wet way. Both processes may be conducted in various ways; and according to circumstances, as one or other of the methods may be more convenient, a considerable number of them are described here.

If the substance contains oxygen, this is estimated from the loss.

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* Annal. d. Chem. u. Pharm. 116, 28.

I. Methods in the dry way.*

1. *Method suitable, more particularly, to determine the sulphur in non-volatile substances poor in sulphur, such as the so-called protein compounds* (LIEBIG).

Some lumps of hydrate of potassa free from sulphuric acid (§ 66, 6, *c*, vol. I.) are put into a capacious silver dish, $\frac{1}{8}$ of pure nitrate of potassa is added, and the mixture fused with the addition of a few drops of water. When the mass is cold, a weighed quantity of the finely pulverized substance is added to it, again fused over the lamp, stirred with a silver spatula, and the heat increased, continuing the operation until the mass becomes white, showing that the carbon separated at first is completely consumed. If this does not take place quickly, some nitrate of potassa is added in small portions at a time. The mass is allowed to cool, dissolved in water, the solution supersaturated with hydrochloric acid in a capacious beaker covered with a glass dish, and finally precipitated with chloride of barium. The precipitate is well washed with boiling water, first by decantation, and then on the filter; dried and ignited. The ignited sulphate of baryta is treated as directed § 132, vol. I.; if this latter operation is omitted, the result is almost always too high. As error may arise from the sulphur present in coal gas, it is better to use a BERZELIUS' spirit lamp; moreover, as it is not by any means easy to obtain reagents perfectly free from sulphuric acid, it is advisable to make a blank analysis with similar quantities of hydrate and nitrate of potassa and hydrochloric acid; if any sulphate of baryta is obtained, the amount is deducted from that found in the actual analysis.

2. *Method adapted more particularly for the analysis of non-volatile or difficultly volatile substances containing more than* 5 *per cent. of sulphur* (KOLBE †).

A layer, 7—8 cm. long, of an intimate mixture of 8 parts of pure anhydrous carbonate of soda with 1 part of pure chlorate of potassa is introduced into the hinder part of a straight combustion tube, 40—45 cm. long, sealed and rounded at the end,‡ after this the weighed substance, then another layer, 7 or 8 cm. long, of the oxidizing mixture; the organic compound is intimately mixed with the carbonate of soda and chlorate of potassa, by means of the mixing wire (fig. 32, § 175), and the still vacant part of the tube is filled up with anhydrous carbonate of soda or potassa mixed with a little chlorate of potassa. A *wide* passage is cleared from end to end by a few gentle taps, the tube placed in a combustion furnace, the fore part heated to redness, and then that part which contains the mixture, advancing the heat slowly to the sealed end. In the analysis of substances containing much carbon, it is advisable to introduce a few lumps of pure chlorate of potassa into the hinder part of the tube, so as to insure complete combustion of the carbon, and the perfect conversion into sulphates of any compounds of potassa with the lower oxides of sulphur that may have been formed. The sulphuric acid in the contents of the tube is determined as in 1; the solution must be evaporated to dryness with excess of hydrochloric acid, &c., so as to separate the silica taken up from the glass.

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* Besides the methods given in the text, there are many others which can here merely be referred to—viz., HEINTZ (Pogg. Annal. 85, 424), Annal. d. Chem. u. Pharm. 136, 225, R. OTTO (Zeitschr. f. anal. Chem. 7, 117), W. F. GINTL (*Ib.* 7, 302), MULDER (*Ib.* 9, 271), &c. A. MITSCHERLICH's method will be explained in § 192.

† Supplemente zum Handwörterbuch der Chem. 1. Aufl., 205.

‡ Instead of this mixture J. T. HOBSON employs one of chlorate of potassa and carbonate of magnesia (Journ. Chem. Soc. 10, 55).

3. *Method adapted for the analysis both of non-volatile and volatile substances, but more especially the latter* (DEBUS *).

1 eq. (149 parts) of dichromate of potassa purified by recrystallization and 2 eq. of carbonate of soda (106 parts) are dissolved in water, the solution evaporated to dryness, the lemon-coloured saline mass ($KO,CrO_3 + NaO, CrO_3 + NaO, CO_2$) reduced to powder, heated to intense redness in a Hessian crucible, and transferred whilst still hot to a flask (fig. 29, § 175).† When the powder is cold, a layer of it, 7—10 cm. long, is introduced into an ordinary combustion tube, then the substance, and after this another layer, 7—10 cm. long, of the saline mixture. This is all intimately mixed by means of the mixing wire, the still unoccupied part of the tube is filled with the saline mixture, and the tube heated as in an ordinary ultimate analysis. When the entire mass is red hot, a slow stream of dry oxygen gas is passed over it for half an hour or an hour. When cold, the tube is cleansed, cut into several pieces over a sheet of paper, and treated in a beaker with a quantity of water sufficient to dissolve the saline mass. Hydrochloric acid (absolutely free from sulphuric acid) is now added in tolerable excess, then some alcohol, and a gentle heat applied until the solution shows a fine green colour; the sesquioxide of chromium produced by the combustion (containing sulphuric acid) is filtered off, washed first with water containing hydrochloric acid, then with alcohol, dried and transferred to a platinum crucible; the filter ash is added, the whole is mixed with 1 part of chlorate and 2 parts of carbonate of potassa (or soda), and then ignited until the sesquioxide of chromium is completely converted into alkaline chromate. The fused mass is dissolved in dilute hydrochloric acid, and reduced by heating it with alcohol; the solution is added to the filtrate from the sesquioxide of chromium, and the sulphuric acid precipitated from the boiling solution by chloride of barium (§ 132, 1, vol. I.). DEBUS' test-analyses were very satisfactory; thus he obtained 99·76 and 99·50 of sulphur for 100; again, 30·2 of sulphur in xanthogenamide instead of 30·4, &c.

4. *Method which can be used for the analysis of either solid or liquid volatile compounds.* (W. J. RUSSELL‡; suggested by BUNSEN.)

In the first place, 2—3 grams pure oxide of mercury are introduced into a combustion tube, 40 cm. long, sealed at one end; then a mixture of equal parts of oxide of mercury and pure anhydrous carbonate of soda, mixed with the substance; the rest of the tube is filled with carbonate of soda containing a little oxide of mercury. The open end of the tube is then connected with a gas delivery tube dipping under water, so as to condense the mercurial fumes. A screen is first placed in front of the part of the tube where the substance is; the fore part is then heated to bright redness, and kept at that temperature during the operation. At the same time, another portion of the tube, nearer to the end, is heated, but not so strongly, so that there may be alternate parts in the tube in which the oxide of mercury is left undecomposed. When the part before the screen is red hot the screen is removed, and the mixture containing the substance is heated in such a manner that it is completely decomposed in the course of 10—15 minutes; at the same time the unheated parts of the tube are heated, and lastly the pure oxide of mercury at the extreme end. The gas must be tested from time to time to ascertain whether it contains free oxygen. The contents of the tube are dissolved in water, some chloride of mercury added, to decompose any sulphide of sodium which may have been formed; it is then acidified with hydrochloric acid, the sulphide of mercury which may have formed is oxidized with chlorate of potassa, and finally the sulphuric acid is precipitated with chloride of barium (§ 132, 1, vol. I.). The results which Russell obtained by this method, in the analysis of pure sulphur, sulphocyanide of potassium, and bisulphide of carbon, were very satisfactory.

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* Annal. d. Chem. u. Pharm. 76, 90.

† The saline mass must first of all be tested for sulphuric acid. For this purpose a small portion of it is reduced with hydrochloric acid and alcohol, chloride of barium added, and the solution allowed to remain at rest for 12 hours; no trace of precipitate should be discernible.

‡ Journ. f. prakt. Chem. 64, 230.

5. *Methods depending on the combustion of the substance in oxygen gas.*

Under this head come methods proposed by C. M. Warren,* W. G. Mixter,† A. Sauer,‡ and G. Brügelmann.§ They have the advantage of yielding the sulphur as sulphuric acid in a liquid containing little other matter, yield excellent results, and are adapted for organic substances of all kinds. I may add that Warren's method allows of the estimation of carbon, hydrogen, and chlorine, as well as that of the sulphur, whilst Brügelmann's provides for the sumultaneous estimation of sulphur, chlorine, and phosphorus in one portion of the substance.

a. Warren uses a combustion tube open at both ends, the posterior third part of which is bent upwards at an obtuse angle; the substance is contained in this part of the tube, and is heated by a special gas lamp. The mixture of the products of combustion with excess of oxygen passes first through a long layer of asbestos, an empty space of 6 cm. follows, then a dense plug of asbestos, then a layer of asbestos with binoxide of lead (which is only heated strongly enough to prevent water from condensing in it), finally there is another plug of asbestos. After the combustion, the whole of the sulphur will be found in the binoxide of lead in the form of sulphate of lead. The mixture of the latter with excess of binoxide and asbestos is digested with a strong solution of bicarbonate of soda for 24 hours, by which the sulphate of lead is decomposed; the sulphuric acid in the filtrate is estimated according to § 132, 1, vol. I.

b. Mixter uses oxygen mixed with bromine vapour contained in a bottle holding from 4 to 10 litres. The combustion tube is similar to Warren's. The apparatus is closed in itself, so that the brominated oxygen circulates continuously. The circulation is produced by heating the ascending part of the tube containing the substance. By rinsing all parts of the apparatus, a solution is finally obtained containing all the sulphur in the form of sulphuric acid, together with hydrobromic acid and some free bromine. The sulphuric acid is estimated according to § 132, 1, vol. I.

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* Zeitschr. f. anal. Chem. 5, 169.

† *Ib.* 12, 212.

‡ *Ib.* 12, 32 and 178.

§ *Ib.* 15, 1 and 175; 16, 1.

c. Sauer's apparatus is comparatively simple, and may be described in detail. The substance is burnt in a current of oxygen, and the sulphurous acid produced is received in hydrochloric acid containing bromine; the greater part of the hydrochloric acid and free bromine is then driven off by evaporation, and the sulphuric acid is estimated according to § 132, 1, vol. I.

a. For substances which when heated give off but little vapour and especially no sulphur, such as coke, the process is extremely simple. The apparatus is shown fig. 63.

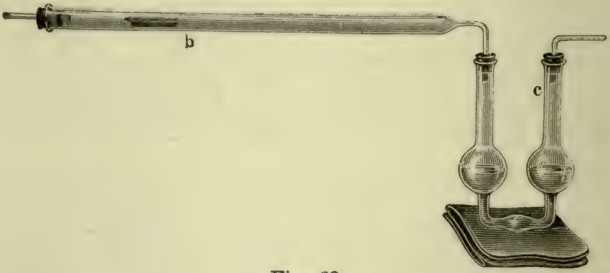

Fig. 63.

The combustion tube, which is from 60 to 80 cm. long, is placed in a furnace; at *b* is a porcelain boat containing the substance. The receiver *c* contains brominated hydrochloric acid. A current of purified oxygen is passed through the tube, which is then heated to redness at *b*. The bromine which escapes from *c* is reabsorbed in hydrate of lime or dilute hydrochloric acid to prevent its occasioning annoyance. As soon as the combustion is over, any condensed liquid is driven into the absorption apparatus *c*, and the tube is swept clean with a current of oxygen or air.

As, even after passing oxygen or air, small quantities of anhydrous sulphuric acid will sometimes remain in the fore part of the combustion tube, it is advisable to rinse the tube with water, and add the washings to the contents of the receiver (F. Muck*).

The ash remaining in the boat may be weighed, and the sulphuric acid in it estimated by treating it at once with hydrochloric acid, unless there is too much oxide of iron present, when it must be fused with the carbonates of potassa and soda (§ 132, II, vol. I.).

β. For substances which volatilize with or without decomposition, the apparatus employed is more complicated. It is shown fig. 64.

The combustion tube, about 85 cm. long, is constricted at *b* to 5 mm. The substance, which is assumed not to be volatile unless heated, is contained in the porcelain boat *d*; the combustion tube lies in a furnace; the tube *xx*, which delivers oxygen, is supported by being fixed to the outside of the furnace; it is somewhat widened at *b*. The flexible tube

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* Zeitschr. f. anal. Chem. 14, 16.

z can be connected at will with an apparatus for delivering dry carbonic acid, or pure oxygen or pure air. The receiver *y*, containing brominated

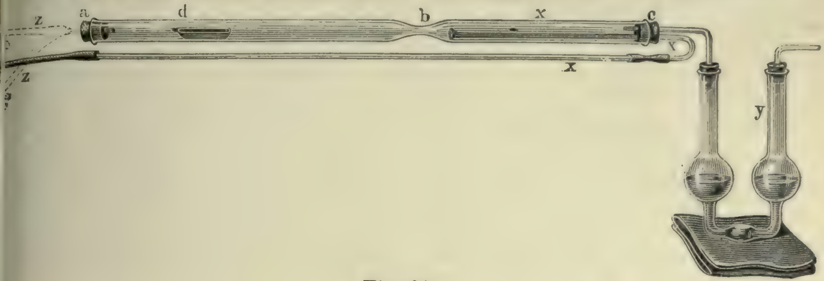

Fig. 64.

hydrochloric acid, is connected with an apparatus containing hydrate of lime or dilute hydrochloric acid to retain escaping bromine. According to SAUER's directions, the space between *d* and *b* is to be kept empty. The author believes, however, it would be advisable to fill it, at least partly, with ignited asbestos, as has been recommended for similar operations by WARREN* and himself.†

When the apparatus is arranged, *b* is heated to bright redness, a gentle current of oxygen is passed through *xx*, a very gentle current of air‡ is allowed to pass through *z*, and the substance is gradually heated.

The evolved vapours meeting the oxygen at the red-hot part *b* are burnt: when this begins, care must be taken that the supply of oxygen is in excess.

When no more vapours are given off and *a b* has been made red hot from *a* to *b*, the current of air is somewhat increased until no more combustion is to be seen at *b*, and oxygen is then passed through *z* instead of air to burn the residue in the boat and any unburnt matter adhering to the tube.

The substance should be cautiously heated so as to prevent any tarry products collecting between *b* and *c*. If, however, any such have been formed they must be finally burnt in the current of oxygen.

It must not be forgotten that a portion of the sulphur may remain in the boat in the form of sulphate, occasionally of sulphide; thus in the analysis of vulcanized india-rubber, sulphide of zinc is often found in the residue. The residue in the boat is therefore dissolved in brominated hydrochloric acid, and the sulphuric acid therein is estimated either by itself or along with that formed in the receiver.

γ. For estimating sulphur in coal gas, this process may also be used. The apparatus is first filled with carbonic acid; the measured quantity of gas is passed into the combustion tube and burnt at *b* in oxygen; finally carbonic acid is again passed through the apparatus until the gas is all expelled and burnt.

δ. For easily volatile fluid substances, such as bisulphide of carbon, the substance is weighed in an apparatus, such as shown fig. 65, made of glass tube 5 or 6 mm. in bore. The tube is first weighed empty and open, then filled, sealed at both ends, and weighed again. The hinder part of the combustion tube is rather closely packed with some broken fragments of porcelain, the apparatus is then filled with carbonic acid, and one end of the U-shaped tube (which must be drawn out thin) is inserted into the air-tight perforated cork. As soon as *b* is red hot, oxygen is passed through *xx*, the U-shaped tube is pushed farther in so that the point is broken off by the porcelain boat, and the fluid gently warmed, so that it may slowly evaporate. In this and in the previous case, the author considers that a layer of asbestos between *d* and *b* is absolutely necessary. When the whole of the fluid has been evaporated, the exterior point of the U-shaped tube is inserted into the flexible tube delivering carbonic acid, the point broken off within the flexible tube, and a slow current of carbonic acid passed until there is no longer any sign of combustion at *b*.

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* Zeitschr. f. anal. Chem. 3, 272.

† *Ib.* 3, 339.

‡ SAUER does not direct this, but the author strongly advises it; otherwise products of dry distillation may readily penetrate to *a*.

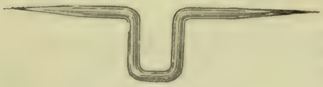
Fig. 65.

d. G. BRÜGELMANN likewise burns the substance in a combustion tube open at both ends, but absorbs the products of combustion in a short layer of granular quicklime or pure granular soda-lime * (4 parts pure lime and 1 part pure hydrate of soda).

Much depends on the quality of the lime. Occasionally the commercial lime from marble may be used, especially if the small quantity of sulphuric acid it contains is estimated and taken into account. Generally, however, it will be better to prepare one's own lime. For this purpose some lime from marble is slaked, and pure nitric acid added, keeping a part of the lime undissolved, and the reaction therefore alkaline. Without filtering, the whole is then evaporated over the naked flame until the boiling point exceeds 140°. The boiling solution will then be covered with a crust of nitrate of lime. This is mixed in a beaker with 2 measures of a mixture of 2 vols. absolute alcohol and 1 vol. ether, stirring up well, and is allowed to settle 12 hours in a closed flask; the pure solution of nitrate of lime is then transferred to a porcelain dish, and the ether and alcohol cautiously driven off, continuing the evaporation with stirring to complete dryness. The nitrate of lime is kept in a well-closed bottle. A portion of the salt is transferred to a pear-shaped porcelain vessel, not glazed inside, and heated to redness in a suitable furnace. As soon as the nitrate is decomposed and the evolution of gas has ceased, a fresh quantity of the salt is added, and the process repeated until the vessel is filled with quicklime. The vessel is then broken, the pieces of porcelain picked out, and the lime broken up in a porcelain mortar until the largest grains have a diameter of about 5 mm.; finally, the fine powder is removed by a sieve of 1 mm. mesh. If commercial lime is used without purification, it is to be granulated in the same way.

The details of the method vary somewhat with the nature of the substance.

a. Solid substances, whether volatile or not.—The combustion tube should be about 50 cm. long and 12 mm. wide. In the end farthest from the oxygen gasometer a roll of platinum foil fitting the tube closely is first inserted, leaving about 2 cm. of the tube empty, then 10 cm. of granular quicklime or soda-lime are filled in, a few taps given to the tube to settle the layer of lime, the tube is cleaned from lime, and the layer of lime plugged in by a second roll of platinum foil, or—for substances containing phosphorus—by 5 cm. of small fragments of broken glass. If the substance is such that the formation of explosive gases may possibly occur, 15 or 20 cm. of ignited asbestos are now put in, and then the substance in pieces (for instance, in the case of parts of plants) or in a boat; the last 15 cm. of the tube remain empty. The hinder part of the tube should project 3 cm. from the furnace, and the sheet-iron trough in which the tube rests should underlie only the lime, the platinum roll (or the broken glass), and 1 cm. of the asbestos. Where the substance has to be used in large quantities, and is placed directly into the tube without a boat, the oxygen tube, the orifice of which is only 5 mm. wide, is connected, and the stream of oxygen is regulated so that it may always be in excess; otherwise the whole of the sulphur will not be converted into sulphate of lime. As a rule, the rate at which the oxygen passes should be, say, 100 c. c. a minute. The anterior 5 cm. of lime are now heated to redness, then the other 5 cm. slowly, and finally the substance as directed below. If a boat is used, the whole layer of lime, the broken glass or platinum foil, and 1 cm. of the asbestos is first heated to redness, then begin to pass the oxygen, remove the hinder plug, insert the boat, and close the tube without loss of time.

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* Zeitschr. f. anal. Chem. 15, 175, and 16, 1.

In burning the substance, begin by cautiously heating it, and take care that there is always excess of oxygen, applying a glowing match to the exit of the tube from time to time.* The lime, if possible, should remain quite white during the whole combustion, and, if the substance begins to glow (burning with a flame is to be avoided), the gas must be turned out under the substance until the glowing ceases. The combustion may also be regulated by diminishing the current of oxygen. Finally the whole remaining part of the tube is heated slowly to redness, proceeding from back to front. As soon as this is done, the carbon burnt, and oxygen is plainly to be detected at the exit, the operation is finished. If a layer of asbestos has been employed, crack the hot tube with a drop or two of cold water where the broken glass or platinum roll joins the asbestos; if asbestos has not been used, the whole of the tube is subjected to the subsequent treatment.

The piece of tube, or the whole tube, as the case may be, is first cleaned externally, the platinum roll at the exit of the tube is removed, and the 2 cm. of lime next to it is emptied into a clean beaker, dissolved in pure dilute hydrochloric acid, and tested for sulphuric acid. If any is found, the analysis is rejected. If none is found, what is left in the tube (with the exception of the other platinum roll and boat, which can be rinsed in the tube) are transferred to a beaker, treated with water and hydrochloric acid (if necessary with addition of bromine), filtered, and the sulphuric acid estimated in the solution according to § 132, 1, vol. I.

β. Liquid volatile substances are weighed in a small thin glass bulb with long thin neck (§ 180): its total length should be 8 cm. The point should be sealed as soon as the bulb is filled. The combustion tube is charged as in *a*, the layer of asbestos being 20 cm. long. When this has been introduced, the tube is heated in the lamp and constricted immediately behind it. As soon as the lime and the part of the tube containing the platinum foil or broken glass and 1 cm. of asbestos are red-hot, the sealed bulb is inserted with the point towards the narrowed part of the tube. The tube is then closed behind with a caoutchouc stopper perforated to carry the oxygen tube; the latter should be of stout glass, and the end delivering the oxygen must be melted and rounded before the lamp until the opening is only ·5 mm. in diameter. The perforation in the stopper should be well greased. The oxygen is turned on, and the oxygen tube pushed forward to break off the point of the bulb. The bulb is first pushed forward until it is 4 cm. from the constricted part of the combustion tube, and the oxygen tube is then drawn back to its original position, so that only a few mm. project through the stopper on the inside. The bulb must be heated with great caution, and very gradually in proportion to the volatility of the substance. As soon as all the fluid is out of the bulb, it is crushed by pushing in the oxygen tube; this is then drawn back again to its proper position, and finally the whole combustion tube is heated to redness, proceeding slowly from the back to the front and the analysis completed as in *a*.

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* If the substance is liable to yield products of decomposition which may give rise to explosions, it should be heated first in a current of air to drive them into the asbestos before turning on the oxygen (Zeitschr. f. anal. Chem. 16, 1).

γ. Estimation of sulphur in coal-gas.—The combustion tube is arranged as in *a*, with an asbestos layer 20 cm. long. The hinder orifice of the combustion tube is closed with a caoutchouc stopper bearing two glass tubes with narrow exits. These tubes should only reach a little beyond the stopper inside. When the fore part of the combustion tube is hot, a current of oxygen is passed through one of the tubes at the rate of 110 or 120 c. c. a minute, and then the coal-gas which has been collected in a glass globe of known capacity, or the gas may be passed through a meter. Long flexible tubes should be avoided for coal gas, and the stream of oxygen must be so regulated as to be always in excess. If a flame appears at the exit of the combustion tube, the current of coal gas must be at once reduced. The combustion takes place at the beginning of the heated part of the tube, and does not extend to the asbestos unless the operation goes on too quickly. About 10 litres of gas should be burnt, which can be done very well in an hour and a half or two hours. Finally the asbestos is heated to redness and the combustion stopped as soon as oxygen can be distinctly detected at the exit. The further treatment is described in *a*. The original paper contains all details as to measuring the gas, &c.

6. *Method for estimating sulphur in coal and coke.*

Eschka* recommends the following comparatively simple method. About 1 gram of the substance in the state of the finest possible powder is intimately mixed in a platinum crucible by means of a glass rod with 1 gram of calcined magnesian and ·5 gram anhydrous carbonate of soda. The crucible, uncovered and supported in an oblique position, is now heated over a spirit lamp, so that the lower half only is red-hot, and the mixture is continually stirred with a platinum wire to promote the combustion, which lasts three-quarters of an hour or an hour. When the carbon has been burnt and the gray colour has become yellowish or brownish, ·5 to 1 gram of *finely powdered* anhydrous nitrate of ammonia is added and intimately mixed, and the ignition continued for 5 or 10 minutes with the cover on. In this way the oxidation of sulphites, which may have been formed at first, is insured.

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* Zeitschr. f. anal. Chem. 13, 344.

The mixture, which has retained its pulverulent form, is now transferred to a beaker, the crucible rinsed, and the whole, which may be about 150 c. c. in volume, is warmed, filtered, acidified with hydrochloric acid, and precipitated with chloride of barium (§ 132, 1, vol. I.). If the magnesia contains a small quantity of sulphuric acid or carbonate of soda this must be estimated and allowed for. Instead of igniting with nitrate of ammonia, the product of the first ignition may be at once dissolved in brominated hydrochloric acid.

By this process, as by all those previously given, the total sulphur of the coal is obtained, including that possibly present as sulphate of lime. If it is desirable to eliminate the latter when present, the finely powdered weighed substance should be boiled for 24 hours with an equal weight of carbonate of soda dissolved in water. This will decompose the sulphate of lime, but leave the sulphide of iron untouched. Filter, wash with boiling water, and use the residue for the estimation of sulphur. The sulphuric acid contained in the sulphate of lime may be estimated in the filtrate (F. C. CALVERT).*

II. Methods in the Wet Way.

1. According to BEUDANT, DAGUIN, and RIVOT,† the sulphur in many organic bodies may be readily determined by heating them with pure potash solution, adding 2 volumes of water and passing chlorine into the liquid. When the oxidation is completed, the solution is acidified, freed from the excess of chlorine by heat, filtered, and then precipitated with chloride of barium. C. J. MERZ has employed this method in the author's laboratory for the analysis of fine horn shavings, and also LIEBIG's (I. 1, p. 57). The results show that the process is both convenient and accurate.‡

2. CARIUS' METHOD. This chemist has made the determination of sulphur (phosphorus, chlorine, bromine, iodine, arsenic, and metals) the subject of careful and comprehensive investigation. To him, we owe the following method, which in skilful hands is not difficult, and which depends on heating the substance in a sealed tube with nitric acid. The very numerous test analyses leave nothing to be desired as regards accuracy.

When CARIUS first published§ his method, he recommended the use of nitric acid of 25 to 60 per cent. As, however, many sulphur compounds, and especially sulphonic acids, are not fully oxidized, or only with difficulty, he advised neutralizing the nitric acid solution with carbonate of soda, and fusing with excess of the latter; subsequently‖ he adopted dichromate of potassa and nitric acid of 1·4 sp. gr. for the oxidation of such refractory bodies; and finally¶ he returns to nitric acid alone, using it of 1·5 sp. gr., which at 200—320° fully oxidizes all bodies. At this temperature, the acid itself suffers decomposition to a large extent into oxygen, water, and nitrous anhydride. To effect the complete oxidation of a substance, from one and a-half to twice the theoretical quantity of nitric acid is sufficient; moreover, it is disadvantageous to use any considerable excess of acid. Thus, for ·24 gram methyl mercaptan, one of the substances requiring the largest amount of oxygen, only 3·3 or at most 4·4 grams nitric acid should be used.

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* Chem. News, 24, 76.

† Compt. rend. 1853, 835; Journ. f. prakt. Chem. 61, 135.

‡ Two experiments by each method were made on horn dried at 100°. The percentages obtained were as follows: by LIEBIG's method, 3·37 and 3·345; by the other method, 3·31 and 3·33.

§ Annal. d. Chem. u. Pharm. 116, 11.

‖ *Ibid.* 136, 129; Zeitschr. f. anal. Chem. 4, 451.

¶ Ber. d. deutsch. chem. Gesellsch. 3, 697; Zeitschr. f anal. Chem. 10, 103.

Substances of course vary in the ease with which they are oxidized; thus, with many compounds, heating for an hour at a maximum temperature of 150—200° will suffice; others—for instance, those of the aromatic series—take one or two hours at 250—260°, whilst the difficultly oxidizable sulphonic acids and their derivatives require either several hours at 250—260°, or a short time at 300°.

In carrying out the process certain rules have to be carefully observed.

The experimental tube is made of ordinary combustion tubing 13 mm. wide and 45 to 50 cm. long, the thickness of the glass being 1·5 to 2 mm. To avoid the risk of an explosion, the quantity of nitric acid should never exceed 4 grams for a tube of 50 c. c. capacity.

The substance is weighed in the tube shown full size fig. 66.

A proper quantity of nitric acid is weighed off and transferred to the experimental tube already containing the weighing tube and substance; the outside tube is then drawn out to a thick-walled capillary tube and sealed.

The heating is regulated by the nature of the substance: an hour and a-half will generally be long enough, in addition to the first half-hour which is spent in raising the tube to the required temperature.

The tubes are heated in a sheet-iron air bath (fig. 67), the glass tubes being inserted in iron tubes; the latter are loosely closed in front and the openings directed towards the wall of the laboratory, or, better, the whole bath should be covered with a wooden box, so that in the event of an explosion no damage may be done.

When the heating is over and the tube is cold, the point is first cautiously warmed to drive back any liquid in it, and the extreme point is then heated to redness so as to blow it out and allow the gases to escape. If there is any doubt whether the oxidation is complete or not, the point is sealed again as soon as the gases have escaped, and the tube is replaced in the bath. The operation of blowing out is also to be recommended, when refractory substances have to be heated at 300° and it is doubtful whether the tube will bear the pressure if the heating is done all at one time.

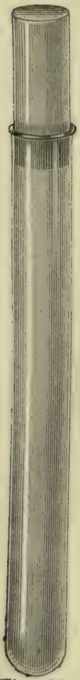
Fig. 66.

Finally rinse the acid fluid out of the tube, dilute and estimate the sulphuric acid according to § 132, 1, vol. I. Kulz* (on the occasion of estimating sulphur in gall) advises evaporating the contents of the tube repeatedly with concentrated hydrochloric acid to remove nitric

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* Zeitschr. f. anal. Chem. 11, 353.

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acid, then to extract with water, filter, and precipitate with chloride of barium.

3. After A. H. Pearson.* The weighed substance is heated in a porcelain dish with pure nitric acid of 1·36 sp. gr., chlorate of potassa is added and the mixture gently warmed, the dish being covered with a well-fitting glass funnel of suitable size, the neck of which is bent at a right angle; fresh quantities of chlorate are added from time to time, and the heating continued until the oxidation is complete. The quantity of chlorate required and the time necessary will depend on the nature of the substance: 1 gram of sulphocyanide of potassium requires, for instance, only 5 or 10 minutes, whilst the same quantity of sulphur requires three quarters of an hour to an hour. The sulphuric acid is estimated in the solution according to § 132, 1, vol. I. The method, of course, is not applicable to volatile bodies.

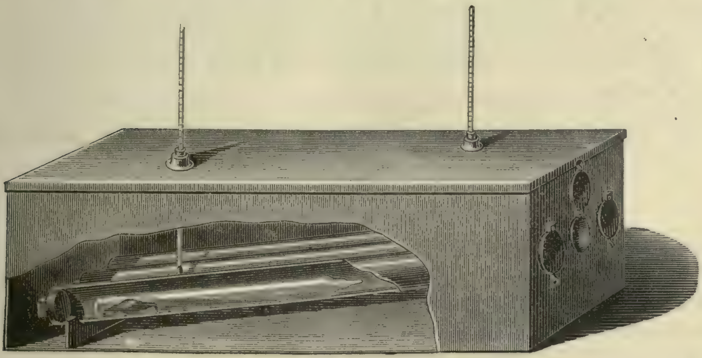

Fig. 67.

Substances which leave an ash on burning may contain part of the sulphur present in the form of sulphates. This must be estimated, and deducted from the total quantity. The estimation of this in the case of coal has been already given (p. 65); in other substances, the same end may be attained by boiling them with hydrochloric acid to dissolve out the sulphates. The sulphuric acid is then determined in the solution according to § 132, 1, vol. I.

D. Estimation of Phosphorus in Organic Bodies.

§ 189.

The estimation of phosphorus is effected in a manner similar to that of sulphur—that is, the substance is oxidized in the dry or wet way, and the phosphoric acid produced is determined.

The methods § 188, I. 1, 2, 4, and 5 *d*, also II. 2, are specially suited for the oxidation. The phosphoric acid is either precipitated directly from the solution as phosphate of magnesia and ammonia, or separated by molybdic acid (§ 134, *b*, *a*, and *β*), after any hydrochloric acid which may be present has been removed by evaporating with nitric acid.

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* Zeitschr. f. anal. Chem. 9, 271.

Phosphorus cannot be estimated in an organic substance by incinerating and determining the phosphoric acid in the ash; thus vitellin, when oxidized by nitric acid, gives 3 per cent. phosphoric acid, but when incinerated it leaves only ·3 per cent. ash (v. BAUMHAUER).

If a body contains phosphates as well as phosphorus in organic combination, a separate portion is boiled with hydrochloric acid, filtered if necessary, and the phosphorus present as phosphoric acid estimated in the solution; its amount is deducted from the total quantity of phosphorus.

E. ANALYSIS OF ORGANIC BODIES CONTAINING CHLORINE, BROMINE, OR IODINE.

§ 190.

In the combustion of organic substances containing chlorine with oxide of copper, subchloride of copper is formed, which, if the process were conducted in the usual manner, would condense in the chloride of calcium tube, and thus vitiate the hydrogen determination. This and every other error may be prevented by using chromate of lead (§ 176); in that case, the chlorine is converted into chloride of lead, and retained as such in the combustion tube.

If the substance is burnt with oxide of copper in a current of oxygen, the subchloride of copper is decomposed by the oxygen, oxide of copper and free chlorine being formed; the latter is retained partly in the chloride of calcium tube, partly in the potash bulbs. To remedy this defect, STÄDELER* proposes to fill the fore part of the tube with bright copper turnings; these must be kept at a gentle red heat during the combustion, and the current of oxygen must be arrested the moment they begin to oxidize. According to A. VOELCKER, the evolution of chlorine may be easily prevented by mixing the oxide of copper with one-fifth of oxide of lead. KEKULÉ recommends placing a few lumps of fused chromate of lead in the fore part of the tube.

K. KRAUT † proposes to modify STÄDELER'S process by placing a roll of silver foil about 15 cm. long, in the fore part of the tube; oxygen may then be passed without fear until it begins to escape from the potash bulbs. This modified process is suitable also for bodies containing bromine and iodine. Where iodine alone is present, it is needless to use metallic copper as well as silver. The silver may be used over and over again before requiring ignition in a current of hydrogen.

GORUP-BESANEZ,‡ when burning dibromotyrosine with chromate of lead, with a mixture of chromate of lead and chromate of potassa, or with oxide of copper and oxygen, always obtained too little carbon, because the lead bromide first formed fused and enclosed carbon, thus shielding it from oxidation. Correct results for the carbon were obtained, however, by employing a combustion tube drawn out to a long point; a layer of oxide of copper 9 cm. long was first introduced, then a plug of asbestos, then a mixture of the finely powdered substance, with about an equal weight of well-dried oxide of lead in a porcelain boat; again a plug of asbestos, then granulated oxide of copper, and lastly chromate of lead or metallic copper. First the foremost and then the hindmost layers are heated to redness, and the part where the porcelain boat lies is very cautiously and gradually warmed; in this way everything combustible distils over, reaches the oxide of copper in the form of vapour, and is there burnt; nothing remains in the boat but a mixture of bromide and oxide of lead. The combustion is completed with oxygen, taking care not to heat the boat too strongly. If silver foil is placed in the very front part of the tube, the hydrogen also will be correct.

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* Annal. d. Chem. u. Pharm. 69, 335.

† Zeitschr. f. anal. Chem. 2, 242.

‡ *Ibid* 1, 438.

The halogens themselves are usually estimated according to one of the following methods.

I. Methods in the Dry Way.

1. *Ignition with lime or soda-lime.*

As lime free from chlorine can easily be obtained by burning marble, it can be employed with advantage for the decomposition of organic substances containing chlorine, bromine, or iodine. It must always be tested for chlorine before being used; and, if traces are found, the amount must be determined in a sample, the analysis of the substance made with a weighed quantity of lime, and a correction made.*

Into a combustion tube about 40 cm. long, sealed and rounded at the farther end like a test tube, a layer of lime, 6 cm. long, is introduced, then the substance, after this another 6 cm. of lime, and the whole is mixed with the wire; the tube is then filled almost to the mouth with lime, a free passage cleared for the involved gases by a few gentle taps, and heat applied in the usual way. Volatile liquids are introduced into the tube in small glass bulbs. When the decomposition is completed, the lime is put into water, dissolved in dilute nitric acid, and precipitated with nitrate of silver (§ 141). It is best to operate as follows:—When the combustion is over, the open end of the tube is closed with a cork, it is cleaned outside, and then immersed whilst still hot, with the sealed end downwards, in a beaker filled two-thirds with distilled water: the tube will break up into small pieces. Nitric acid is now added until the lime is dissolved, the solution is filtered from separated carbon, &c., and precipitated with nitrate of silver. As cyanide of calcium may be formed when very nitrogenous bodies are ignited, the chlorine, bromine, or iodine must be separated according to § 169, 6, vol. I., if necessary.

If the lime contains small quantities of sulphide of calcium (F. Sestini †), the chloride, bromide, or iodide of silver must be separated from the sulphide.

If soda-lime (free from chlorine or containing a known quantity) is used instead of lime, it has the advantage that all carbon is oxidized to carbonic acid, and no cyanide is formed.‡

If this process is used for bodies containing iodine, any free iodine must be converted into hydriodic acid by a few drops of solution of sulphurous acid before adding the nitrate of silver.

With bodies containing iodine, Classen § prefers to pass moist carbonic acid over the mass for several hours after the ignition with lime, then to warm with water, filter, neutralize cautiously with nitric acid, and precipitate the iodine with nitrate of silver. In the analysis of acid compounds (*e.g.*, chlorospiroylic acid), the halogen may often be determined in a simpler manner; it is only necessary to dissolve the substance in excess of dilute potash solution, evaporate to dryness, and gently ignite the residue, when the whole of the chlorine, bromine, or iodine present is converted into a soluble haloid salt (Löwig).

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* Special methods for preparing pure lime free from chloride and sulphide have been given by F. Sestini (Zeitschr. f. anal. Chem. 4, 51) and Brügelmann (*Ibid.* 15, 5).

† Zeitschr. f. anal. Chem. 4, 51.

‡ Handb. d. anal. Chem. von H. Rose, 6. Aufl. von R. Finkiner, 2, 735.

§ Zeitschr. f. anal. Chem. 4, 202.

2. *Ignition with sesquioxide of iron and iron* (E. Kopp*).

The combustion tube used is about 60 cm. long and 5 or 6 mm. wide, sealed at one end. In order to bring the decomposition more under control, the substance is intimately mixed with pure sesquioxide of iron (prepared by igniting the protosulphate in the air), and then introduced into the tube. The layer should be loose and 12 or 18 cm. long. Having added the rinsings, several closely wound spirals of rather fine iron wire are inserted—amounting in all to 20 or 25 cm. in length. The remaining space in the tube is filled with porous crusts of anhydrous pure carbonate of soda, obtained by moderately heating the crystallized salt in a platinum dish.

The part of the tube containing the iron spirals is first heated to redness, and then the mixture, beginning at the front. The halogens are obtained as protosalts of iron; any minute quantities of these which may volatilize are decomposed and retained by the carbonate of soda. When cold, the tube is cleaned, cut up into pieces, and boiled with water for some time; in this way, the iron salts are decomposed by the carbonate of soda. After filtering and washing, the solution is cautiously acidified with nitric acid and precipitated with nitrate of silver.

3. *Combustion in a current of oxygen.*

a. C. M. Warren's† process, already described under the "Estimation of Sulphur" (§ 188, I. 5 *a*), and to which we shall again return (p. 82), is also applied to the estimation of chlorine. The chlorine liberated by the combustion of the substance in oxygen is absorbed by brown oxide of copper (prepared by precipitating a copper salt with potash and igniting over a gas lamp) placed in the fore part of the tube between asbestos plugs. If the carbon and hydrogen are to be estimated along with the chlorine in the same portion of substance, the fore part of the tube containing the oxide of copper must be heated in such a manner that no carbonic acid or water is retained, whilst no chlorine is allowed to escape. Warren effects this by means of an air bath surrounding the part.

Difficultly combustible substances, such as chloroform, require a different treatment, otherwise a difficultly volatile fluid condenses in the vacant space between the hinder layer of asbestos and the layer of oxide of copper and asbestos. In such cases, the asbestos in the hinder part of the tube is mixed with oxide of zinc (say 3 grams), and in the fore part a mixture of oxide of zinc (say 1 gram) and asbestos is placed. The temperature of the air bath should not exceed 160°.

After the combustion, the chloride, with the excess of oxide, is extracted from the asbestos by diluted nitric acid, and the solution precipitated with nitrate of silver.

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* Zeitschr. f. anal. Chem. 15, 107.

† *Ibid.* 5 174.

The test results given by WARREN are quite satisfactory. He thinks it probable that the method would answer also for bromides.

β. G. BRÜGELMANN'S process for the estimation of sulphur (and phosphorus), described § 188, I. 5 *d*, is well adapted also for the simultaneous estimation of the chlorine. Of course the lime must be tested for chlorine. The process is also adapted for the estimation of bromine and iodine, if soda-lime is used instead of lime. When the combustion is ended, and the foremost 2 cm. of lime or soda-lime have been tested to see if they are free from chlorine, the main portion of the lime is dissolved in very dilute nitric acid, which has been first used for rinsing the tube, the parts of the tube which have been attacked by the fused chloride of calcium being digested with the dilute acid for a long time; finally the solution is filtered, and precipitated with nitrate of silver.

The author's test analyses are very satisfactory, since the combustion of the substance is effected by a current of oxygen, as in WARREN'S process. Of course, in the analysis of difficultly combustible bodies, such as chloroform, a modification will be necessary similar to that described under *a*.

II. Methods in the Wet Way.

1. CARIUS' METHOD.[*] As in the case of sulphur determinations, CARIUS has gradually improved the method for estimating chlorine, bromine, and iodine in organic compounds, the substance being digested with nitric acid in sealed tubes. In the latest form of the process, the nitric acid is employed of 1·5 sp. gr., as in the estimation of sulphur, § 188, II. 2; the addition of dichromate of potassa, formerly recommended, is then unnecessary. The operation is precisely similar to that for sulphur, with the single exception that besides the weighed substance and the 4 grams nitric acid a slight excess of nitrate of silver is added. All the chlorine, bromine, and iodine present are separated as silver salts. Neither bromic nor iodic acid can be formed, as the nitrous acid produced would reduce them. Organic substances are decomposed with extraordinary ease in the presence of nitrate of silver, in most cases partially even in the cold. With bodies of the aromatic series, the complete separation of the halogens is more difficult, but a temperature of 250° or 260° is always sufficient. The precipitate of silver salt is filtered off and weighed; before filtering, CARIUS advises the neutralization of the greater part of the free nitric acid with pure carbonate of soda. With bodies containing iodine, it is particularly to be noticed that the iodide of silver unites with the excess of the nitrate and fuses in the hot tube to a yellow compound, which on cooling solidifies to an opaque yellow mass. This must be heated for 1 or 2 hours in the dilute liquid to remove the nitrate: the iodide is then quite pure.

According to LINNEMANN[*] the estimation of iodide is not so satisfactory as that of chlorine or bromine. He refers the losses which he noticed to the fact that iodide of silver is somewhat soluble in the liquid containing nitrate of silver and nitric acid. He therefore advises that a large excess of nitrate of silver should be avoided, $1\frac{1}{2}$ equivalent being sufficient.

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[*] Zeitschr. f. anal. Chem. 1, 240; 4, 451; 10, 103.

[†] *Ibid.* 11, 325.

2. In readily decomposible bodies, such as the substitution derivatives of acids, the halogen may also be determined by treating the substance for several hours with water and sodium amalgam, and (for chlorine and bromine) acidifying with nitric acid and precipitating with nitrate of silver. For iodine compounds, nitrate of silver is first added to the alkaline fluid and then nitric acid to dissolve the precipitated oxide of silver (KEKULÉ*).

3. For estimating the iodine in hydriodate of ethyltropine, K. KRAUT† employed a very simple method, which, moreover, has the advantage of saving the substance. It has also been applied by R. MALY ‡ to the estimation of the extra-radical bromine in a body obtained by the action of bromine on thiosinamine.

An accurately weighed quantity of pure silver is dissolved in nitric acid, diluted, precipitated with hydrochloric acid, decanted through a weighed filter to retain the small portions of chloride of silver in the washings, and the filter washed. The weighed substance is now added to the washed chloride. After a few minutes standing and warming, the whole of the iodine becomes combined with silver, whilst the base unites with hydrochloric acid. The mixed iodide and chloride of silver is collected on the filter first used, washed, dried, and weighed. The iodine is calculated from the difference in weight between this precipitate and the chloride of silver equivalent to the silver employed.

The method only yields the iodine or bromine which is combined in the same way as the chlorine is in chloride of ammonium (MALY).

4. In compounds of hydrochloric, hydrobromic, or hydriodic acid with an organic base, the halogen may be easily estimated by precipitating the aqueous solution with nitrate of silver.

F. ANALYSIS OF ORGANIC SUBSTANCES CONTAINING INORGANIC COMPOUNDS.

§ 191.

In the analysis of organic substances containing inorganic compounds, it is, of course, necessary first to ascertain the quantity of the latter before proceeding to the determination of the carbon, &c., as otherwise, the amount of the organic compound whose constituents have furnished the carbonic acid, water, &c., not being known, it would be impossible to estimate the oxygen from the loss.

If the substances in question are salts or similar compounds, their bases are determined by the methods given in the Fourth Section (vol. I.); but in cases where the inorganic bodies are of a nature to be regarded more or less as impurities (such as the ash in coal), they may usually be determined with sufficient accuracy by the combustion of a weighed portion of the substance in an obliquely placed platinum crucible, or in a platinum dish, with use of a cylinder to promote the draught§ (see "Analysis of Ashes"). If the ash still contains carbon, mix it repeatedly with oxide of mercury, and ignite until the weight is constant. In the analysis of substances containing fusible salts, long-continued ignition, even when oxide of mercury is used, will often fail to effect complete combustion, as the carbon is protected from the action of the oxygen by the fused salt. In such cases, the best way to effect the purpose is to carbonize the substance, treat the mass with water, and incinerate the undissolved residue; the aqueous solution is, of course, also evaporated to dryness, and the weight of the residue added to that of the ash.

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* Jahresb. von KOPP u. WILL, 1861, 832.

† Zeitschr. f. anal. Chem. 4, 167. ‡ *Ibid.* 5, 68.

§ Or, still better, in a muffle.—The EDITOR.

The estimation of inorganic substances in presence of organic is not always so simple as it appears at first sight, for the ash very often does not represent simply the sum of the inorganic bodies; for instance, the bases may have taken up acids produced by the combustion, chlorides may have been dissipated (BEHAGHEL v. ADLERSKRON*), &c. The details will be given under the "Analysis of Ashes."

If organic compounds whose ash contains potassa, soda, baryta, lime, or strontia are burnt with oxide of copper, part of the carbonic acid evolved remains combined with the bases; as, in many cases, the amount thus retained is not constant, and the results are, moreover, more accurate if the whole amount of the carbon is expelled and weighed as carbonic acid, certain bodies are added to the substance before it is mixed with oxide of copper, so as to decompose the carbonates at a high temperature, *e.g.*, teroxide of antimony, phosphate of copper, boric acid (FREMY), &c.; or the substance is burned with chromate of lead, with addition of $\frac{1}{10}$ of dichromate of potassa (§ 176); the latter method is strongly recommended. Accurate experiments have shown that, in this case, not a trace of carbonic acid remains with the bases.

If the substance is weighed in a porcelain or platinum boat, and the combustion made as in § 178, *a*, the ash, carbon, and hydrogen can be determined in one portion. The amount of carbonic acid contained in the ash is added to that found by the combustion; if the carbonic acid in the ash cannot be calculated, it may be determined by using fused borax, by fusion with dichromate of potassa, by PERSOZ'S method, or in some other way (§ 139, vol. I.).

In burning substances which contain mercury, the passage of any of the metal into the chloride of calcium tube may be prevented by having a layer of copper turnings, foil, or wire in the fore part of the combustion tube, and by not allowing the foremost portion to get too hot.

Substances with radicals containing metals, or those which contain volatile metals, may be analysed extremely well by the method of CARIUS (p. 65). The metals are determined in the nitric acid solution produced. If the bodies also contain sulphur, the metals may be separated with carbonate of soda (supposing, of course, that they are precipitable by this reagent), and the sulphuric acid determined in the filtrate.

For substances containing chlorine, bromine, or iodine, the silver must be precipitated from the filtrate by hydrochloric acid, and the metal subsequently estimated in the clear solution.

In substances containing mercury, the metal may be estimated along with the carbon and hydrogen by a modification of the ordinary process of combustion (FRANKLAND and DUPPA†). Substances containing arsenic may be analysed by BRÜGELMANN'S method for those containing phosphorus (pp. 62, 67 ‡).

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* Zeitschr. f. anal. Chem. 12, 390. † Journ. Chem. Soc. 1863, 417. ‡ *Ibid.* 16, 1.

SUPPLEMENT TO §§ 174—191.

§ 192.

A. Methods for the Direct Estimation of Oxygen.

As already mentioned, the oxygen, in the ordinary method of organic analysis, is determined from the loss. Formerly no method for its direct determination was known, and even now, although we are indeed acquainted with such methods, they are only used exceptionally, as they are troublesome to work, and only yield accurate results when great care is taken. It is remarkable that hardly any of the methods given below have been tested except by their authors.

a. v. **Baumhauer** was the first to suggest a method for the direct estimation of oxygen.* It consisted in employing a measured quantity of oxygen in the ordinary process of estimating carbon and hydrogen, so as to reoxidize the copper reduced in the process. The amount of oxygen in the substance is found by deducting the oxygen absorbed by the copper in the apparatus from that present in the carbonic acid and water.

In an operation by this method, the total cubic capacity of the apparatus requires to be known in order to make the corrections for temperature and pressure, and, as this cannot be readily and accurately ascertained, v. **Baumhauer** now† recommends the use of a weighed quantity of a substance which will yield a definite amount of oxygen on ignition; such as dry iodate of silver, which answers the purpose admirably. This process is adapted not only to the estimation of carbon, hydrogen, and oxygen in one and the same portion of substance, but also—with certain modifications to be described—of the nitrogen present.

The combustion tube is 70 or 80 cm. long, open at both ends, and is charged as follows, beginning in the fore part:—Next the absorption apparatus, 20 cm. copper turnings, 20 cm. broken porcelain (previously washed with hydrochloric acid and ignited), 25 cm. strongly ignited coarsely granulated oxide of copper free from powder, with plugs of asbestos at each end, an empty space of 5 cm., then the substance in a boat or—if liquid—a bulb (if difficultly combustible, it may be mixed with oxide of copper), then an empty space of 6 or 7 cm., and lastly another boat containing a known weight (a few grams) of pure iodate of silver dried at about 140°.‡ A constant hydrogen apparatus and a gasometer containing pure nitrogen are also required. Both gases pass through the same purifying apparatus to the hinder part of the tube. The purifying apparatus consists of a tube filled with copper turnings, kept red hot during the whole experiment, a U tube with pumice saturated with sulphuric acid, and a second U tube filled one half with soda-lime and the other half—next to the combustion tube—with chloride of calcium.

Before attaching the absorption apparatus for water and carbonic acid, the fore part of the tube is heated to a little beyond the turnings, and a slow current of hydrogen is passed through to make sure that the copper is free from oxide or suboxide; the hydrogen is then displaced by nitrogen, the parts of the tube containing the broken porcelain and oxide of copper are heated, keeping up a gentle current of the gas. The chloride of calcium tube and the potash bulbs with their hydrate of potash tube are now connected. After the nitrogen has been passing some time, and all parts of the apparatus are filled with it, the potash solution also being saturated with it, the absorption apparatus is allowed to cool, weighed, and again placed in position. The substance is now heated with great care, a slow current of nitrogen being passed the whole time. When the substance is burnt or fully carbonized, the silver iodate is very gradually heated. The oxygen evolved burns the carbon and oxidizes the copper formed from the oxide by reduction; the excess of oxygen being taken up by the turnings. When the iodate is completely decomposed, a gentle current of nitrogen is passed through the apparatus for some time, and the absorption apparatus is then detached to weigh them. The gas cocks are turned off one by one, except those under the turnings. Without stopping the current of nitrogen, the oxide of copper is allowed to become quite cold, and a fresh weighed chloride of calcium tube is then attached; a current of hydrogen is now passed instead of the nitrogen, to reduce the oxide and suboxide of copper formed on the turnings; the oxygen in these oxides combines with the hydrogen, and is collected and weighed in the chloride of calcium tube. The boat is then drawn out of the tube with a wire, and the apparatus is ready for a fresh analysis.

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* Annal. d. Chem. u. Pharm. 90, 228.

† Zeitschr. f. anal. Chem. 5, 141.

‡ For its preparation see *loc. cit.* p. 143.

The calculation is as follows:—The oxygen in the weighed quantity of iodate of silver* is deducted from the sum of the oxygen in the carbonic acid and the total water (obtained in both chloride of calcium tubes). The difference is the oxygen in the substance.

The test results supplied by v. BAUMHAUER in the analyses of oxalic and uric acids are quite satisfactory.†

In estimating nitrogen in the same portion of substance, the apparatus is arranged as before, but the flexible tube connecting the hinder part of the combustion tube with the U tubes must have a screw clip. The process is the same as above described up to the time when the combustion of the substance is to be commenced. While the nitrogen is still slowly passing, the potash bulbs are connected with a system of tubes, which serves to measure the volume of gas in the whole apparatus before and after the burning of the substance. This system consists of two vertical tubes joined below by a long and very strong flexible tube. One of the tubes is fixed and graduated; the other is suspended by a cord, and can be raised or lowered. Mercury is poured in until it rises half way up these tubes. Before connecting the graduated tube with the potash bulbs, it should be entirely filled with mercury by raising the other tube.

When the mercury has reached the point at which the graduation of the tube begins, the screw clip behind the combustion tube is closed, the tube allowed to cool, and the volume of gas in the apparatus determined by two readings at different pressures, the first at a diminished pressure of 20 mm., the second with the mercury at the same height in both tubes. The substance is now burned as before, but without using a current of nitrogen and without heating the iodate of silver. When the combustion is over and the apparatus has been allowed to cool for several hours, two more readings are taken at different pressures to ascertain the volume of gas in the whole apparatus. The increase is due to nitrogen in the substance. The potash bulbs are now disconnected from the measuring apparatus, the clip behind the combustion tube is opened, and the combustion finished by heating the iodate of silver, &c., as before described.

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* 100 parts of the salt dried at 140° yielded v. BAUMHAUER 16·92 parts of oxygen.

† A. MITSCHERLICH (Elementaranalyse vermittelst Quecksilberoxyds, Berlin, Mittler u. Sohn, 1875; Zeitschr. f. anal. Chem. 15, 371) has observed that it is extremely difficult to reconvert reduced copper completely into oxide by ignition in oxygen, a kernel of suboxide remaining when the grains are of any size; and infers that this will be a serious source of error, especially with substances rich in carbon and hydrogen.

The method of simultaneous nitrogen estimation, although cleverly contrived, is far from perfect, and, as v. Baumhauer himself admits, it can rarely be used. It is generally preferable to estimate the nitrogen in a separate portion of the substance.

b. Stromeyer's Method.*

This process depends on the determination of the metallic copper, or, as the case may be, suboxide of copper, formed in the combustion. The residue is taken up with a solution of sesquichloride of iron and hydrochloric acid, or, better, of sesquisulphate of iron and sulphuric acid, and the protoxide of iron formed titrated with permanganate. $Cu + Fe_2Cl_3 = CuCl + 2\ FeCl$ or $Cu_2O + Fe_2Cl_3 + HCl = 2\ CuCl + HO + 2\ FeCl$. From this it is evident that, no matter whether the oxide of copper is reduced to metal or suboxide, 2 FeO is obtained for each equivalent of oxygen given up. The oxygen in the substance is found by adding together the oxygen contained in the carbonic acid and water, and subtracting from this 1 eq. oxygen for every 2 eq. protoxide of iron. As the oxide of copper employed must be free from suboxide, it is prepared from the basic carbonate of copper by heating it in a glass flask (not in a crucible). The oxide prepared in this way is not so well adapted for the carbon and hydrogen determination, since the carbonic acid and the aqueous vapour are evolved with great rapidity. Stromeyer therefore recommends that the determination of the oxygen should not be combined with the determination of the carbon and hydrogen, but should be performed on a separate portion of substance. As the above oxide of copper is very readily reduced, much less of it is required than of the coarse oxide. Organic bodies which contain enough oxygen to form water with the hydrogen require about three times as much oxide as the theoretical quantity, and bodies which contain an excess of hydrogen require four times as much; to be quite safe, however, somewhat more than this is taken. The oxide of copper is mixed with half its weight of dry carbonate of soda: this mixture agglomerates when ignited, so that the last particles of carbon are burnt. The sulphur in organic substances is burned with this mixture to sulphate of soda—chlorine yields chloride of sodium; and here it must not be forgotten that the oxygen of the soda is expelled, and goes to form carbonic acid and water. In the case of nitrogenous compounds, the method does not answer so well—nitro-compounds yield too much reduced copper, because oxides of nitrogen escape; with other nitrogenous compounds, however, the results are approximate.

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* Annal. d. Chem. u. Pharm. 117, 247.

The substance is mixed with the mixture of oxide and carbonate of soda in a smooth dish with a small spoon, then filled into the tube by means of a small funnel, and as much oxide of copper again is added. The latter is granulated like gunpowder, by making it up to a proper consistence with $\frac{1}{10}$ carbonate of soda and water, passing through a sieve of perforated metal plate with holes of one line diameter, drying, and then sifting off the dust. The combustion tube is connected by means of a cork or caoutchouc tube with a glass tube drawn out to a fine point. After giving the tube a few gentle taps, it is heated as usual, slowly proceeding from the front to the back. When the whole tube is red hot, the opening of the small glass tube is sealed, the combustion tube is allowed to cool, and the contents of the tube—with the pieces of the glass tube, if it cannot be done without—are transferred to a flask. The liquid used to dissolve the copper is a solution of sesquisulphate of iron containing 8 per cent. of sesquioxide of iron, free from protoxide of iron and nitric acid. Double the necessary quantity of this solution is taken (reckoned from the oxygen determined as usual from the loss, which determination is here controlled), and a little more dilute sulphuric acid (prepared from the distilled acid) added than is necessary to saturate the carbonate of soda and to dissolve the oxide of copper. The flask is provided with a MOHR's caoutchouc valve (or a stream of carbonic acid may be passed), and heat is cautiously applied, until the whole of the copper is dissolved; if, in consequence of too violent heating, red specks remain on the glass, the sulphuric acid solution when cold is poured into a litre flask, the fragments of the tube are heated with a small quantity of sesquichloride of iron and hydrochloric acid, and the two solutions are mixed. If the solution after being diluted is not of the colour of sulphate of copper, but yellowish-green, there is a deficiency of sulphuric acid, and some more must be added. Finally, the flask is filled up to the mark with water, mixed, and $\frac{1}{4}$ litre taken for titration; this must be again diluted with $\frac{1}{4}$ litre of water. In order to be able to correct the error which arises from the fact that a fluid containing sulphate of copper and sesquisulphate of iron requires more permanganate to colour it than water, $\frac{1}{4}$ of the weight of the oxide of copper employed (the fine and the granulated) is dissolved in dilute sulphuric acid, $\frac{1}{4}$ of the above-mentioned solution of sesquisulphate of iron added, the whole made up to $\frac{1}{2}$ litre, and the permanganate (diluted tenfold for this purpose) added to distinct redness. The test analyses communicated by the author of the process are satisfactory.* But as in the experiment detailed in the note, there is always too little oxygen used, and consequently the result is too high. The atmospheric air in the tube is probably the main cause of this error, and STROMEYER therefore suggests that more accurate results might be obtained if the air were removed by alternately exhausting and filling with carbonic acid.

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* To render the matter plain the author cites the details of an actual analysis as follows :—·202 gram cane sugar mixed with 3 grams CuO and 1·5 NaO,CO_2, and 3 grams granulated oxide of copper placed in front. Dissolved in 50 c. c. of solution of sesquisulphate of iron of 8 per cent. Fe_2O_3 and 8 c. c. distilled oil of vitriol, and diluted to 1 litre. 250 c. c. thereof, diluted to 500 c. c., required in 2 experiments 48·6 c. c. of a permanganate solution, of which 17·3 c. c. = 1 gram double sulphate of iron and ammonia or ·020408 oxygen, and of which ·9 c. c. were required for reddening a solution of ·75 gram fine and ·75 granulated CuO in dilute sulphuric acid, mixed with 12·5 c. c. solution of sesquioxide of iron and water to $\frac{1}{2}$ litre. Subtract this ·9 from 48·6, the remainder is 47·7, which, when multiplied by 4, gives 190·8 = ·225071 O. This makes for 1 at. cane sugar ($C_{12}H_{11}O_{11}$) 190·5 O instead of 192 (24 at.), which are actually required.

c. A. **Mitscherlich** has been for many years endeavouring to discover a method for estimating all the elements of an organic body in one analysis. For this purpose, he decomposed the substance first by heating it in a current of chlorine,* so that the hydrogen was obtained as hydrochloric acid, and the oxygen as carbonic acid and carbonic oxide, which were determined. The numerous test results supplied give the hydrogen and oxygen very satisfactorily. Subsequently † he used platinochloride of potassium instead of chlorine, so as to be able to estimate the oxygen, hydrogen, and carbon simultaneously, and he improved this method by adding chloride of potassium to the mixture of the substance with the platinochloride. But as in these methods a part of the carbon is converted into chloride, and the estimation of the carbon rendered difficult, he endeavoured to attain the object in another way, and at last succeeded in devising a process adapted for the estimation *in one analysis* of carbon, hydrogen, and oxygen (specially) and also nitrogen, chlorine, bromine, iodine, sulphur, phosphorus, and any inorganic substances which might be present.‡

It consists in burning the substance with oxide of mercury. At the temperature at which oxide of mercury is decomposed by itself, water, carbonic acid, and mercury are formed. The carbon and hydrogen are estimated from the weight of the carbonic acid and water; by weighing the mercury reduced, the amount of oxygen used in the combustion is found, whilst by deducting the latter from the oxygen present in the products of combustion, the amount of oxygen present in the substance is ascertained. Where nitrogen is present, it separates as such or as nitric oxide. Chlorine, bromine, and iodine, if present, unite with the free mercury during the combustion. Sulphur and phosphorus are obtained as sulphate and metaphosphate of mercury. These salts, and almost all other inorganic bodies in the substance, remain with the oxide of mercury, and must be afterwards separated therefrom.

A. **Mitscherlich** has analysed a great variety of substances by this method, generally with excellent results. Other chemists have not examined it.

The method and the necessary apparatus are described in detail by **Mitscherlich**, and, as satisfactory results cannot be obtained without careful observance of the various details, a short summary of the method would be useless.

d. A. **Ladenburg** § oxidizes the substance in a sealed tube with iodate of silver and sulphuric acid. The substance is weighed in a bulb, and placed with pure sulphuric acid and a known quantity of iodate of silver in a tube, which is then drawn out and sealed. The bulb is then broken by striking the tube on one's hand, and the tube is heated. When the reaction is over, and the tube is cold, it is weighed, the point melted to allow the gas to blow out and escape, and the carbonic acid absorbed by the sulphuric acid is removed by heating and exhausting, the tube is again weighed, and the operations repeated until the weight is constant. The loss of weight is equal to the amount of carbonic acid produced, from which the carbon in the substance may be calculated. The tube is now cut open, its contents rinsed out, iodide of potassium is added, and the free iodine estimated (§ 146, vol. I.) : this gives the iodate still undecomposed, from which the oxygen necessary for the oxidation of the substance can be calculated.

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* Zeitschr. f. anal. Chem. 6, 136. † *Ibid.* 7, 272.

‡ *Ibid.* 13, 74; 15, 371; also Elementaranalyse vermittelst Quecksilberoxyds, Berlin, Mittler u. Sohn, 1875.

§ Annal. d. Chem. u. Pharm. 135, 1; Zeitschr. f. anal. Chem. 4, 192.

The results supplied by LADENBURG are on the whole satisfactory.

e. J. MAUMENÉ * burns the substance with litharge mixed with ¼ phosphate of lime, to prevent fusion. Carbonic acid and water are thus obtained as in the ordinary process, and also metallic lead; in order to obtain the latter as a button, the contents of the tube, after the combustion, are mixed with about double the quantity of pure litharge, transferred to a crucible, covered with a layer of pure litharge, and fused. The button obtained is finally cleaned and weighed. The oxygen of the substance is found by adding together that contained in the carbonic acid and water, and subtracting that corresponding with the metallic lead obtained. The author does not state how he avoids the error occasioned by the air in the tube.

f. CRETIER † passes the products of the dry distillation of the substance over a known weight of magnesium heated in a weighed combustion tube, thereby reducing the water and, for the most part, the oxides of carbon, reweighs the tube, and subjects the gas which has escaped from the tube, consisting of hydrogen, hydride of methyl, and possibly carbonic oxide, to a special analysis. From these data, the carbon, hydrogen, and oxygen are calculated, but the results are not satisfactory.

B. METHODS OF ORGANIC ANALYSIS WHICH DIFFER FROM THE ORDINARY PROCESS WITHOUT INCLUDING A DIRECT ESTIMATION OF OXYGEN.

a. CLOËZ ‡ has described a process for estimating carbon, and hydrogen (also nitrogen), which is applicable to solid or liquid, non-volatile or volatile bodies, whether they consist of carbon, hydrogen, and oxygen only, or contain also nitrogen, sulphur, chlorine, bromine, iodine, or inorganic bodies.

The author thought it best to reserve all consideration of this process for the present supplement, so that he might be enabled to present the method in a connected form. The characteristic feature of the method, which in general is modelled after that described in § 178, consists in this, that the glass combustion tube and the oxygen are replaced by a wrought-iron pipe and purified air respectively. In consequence of the first change, the apparatus can be used again and again, and is therefore especially suited for extensive series of experiments of scientific or technical interest. The accuracy of the method has been fully proved by numerous test analyses of the most various kinds. The great majority of the results obtained are thoroughly satisfactory.

The combustion tube *A B* (fig. 68) is of wrought iron, 20—22 mm. in diameter and 115 cm. long. Both ends project 20 cm. from the furnace. The first thing to do is to oxidize the inner surface of the tube

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* Compt. rend. 55, 432; Zeitschr. f. anal. Chem. 1, 487.

† Zeitschr. f. anal. Chem. 13, 1.

‡ Annal. de Chim. et de Phys. Sér. [iii.] 68, 394.

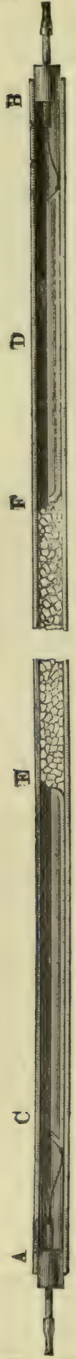

Fig. 68.

by heating it to redness and passing a current of steam through it.* As soon as this is fully accomplished, the middle part of the tube, between *E* and *F*, is filled with a long layer of strongly ignited coarse oxide of copper, keeping it in its place with spirals of copper foil superficially oxidized. The empty portions of the tube, *F B* and *A E*, are destined to receive long semicylindrical boats of strong sheet iron, which can be pushed in and drawn out by means of iron wires fastened to the end of each. The boat in the fore part of the tube at *D* is 20 cm. long; when substances have to be burnt containing carbon, hydrogen, and oxygen only, it is filled with coarse oxide of copper, or, if the substance is readily combustible, it is left out; in the analysis of nitrogenous bodies, the boat is filled with freshly reduced copper turnings, and with red lead or with chromate of lead; the substance contains sulphur or chlorine. The boat to be placed in the hinder part of the tube at *C E* is 30 cm. long. In the combustion of substances containing only carbon, hydrogen, and oxygen, it is filled with moderately ignited oxide of copper; if the substance contains sulphur, chlorine, or bromine, it is filled with fused and powdered chromate of lead. To collect the water produced in the combustion, Cloëz uses a U tube filled with fragments of pumice moistened with sulphuric acid, then follow the potash bulbs and a U tube filled with pieces of hydrate of potassa. The air which is to be passed through the combustion tube is first conducted through a small bottle containing dilute potash solution (the entrance tube only just dipping into the fluid), then through an upright cylinder, narrowed towards the bottom, containing pumice saturated with sulphuric acid (fig. 79, p. 200, vol. I.), then through two long horizontal tubes with turned-up ends, the first of which is filled with porous chloride of calcium, the second with fragments of hydrate of potassa.†

If a solid substance composed entirely of carbon, hydrogen, and oxygen has to be burned, both the boats are filled with oxide of copper, the tube is heated along its whole length, and a slow stream of air is passed for 10 to 15 minutes; the foremost end of the tube remaining open. The part *C E* of the tube is now allowed to cool, the tube is seized with the tongs (fig. 69), the stopper *A* removed, the boat taken out and allowed to cool in a closed iron tube kept for the purpose, or, if more convenient, it may

Fig. 69.

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* This is of great importance, since it appears to destroy the very notable permeability of red-hot iron observed by Sainte-Claire Deville and Troost (Compt. rend. 57, 965; Zeitschr. f. anal. Chem. 3, 351) and Cailletet (Compt. rend. 58, 327 and 1057; Zeitschr. f. Anal. Chem. 3, 353).

† This arrangement of the drying apparatus is incorrect. The air entering the combustion tube is dried by chloride of calcium, whilst it leaves it dried by the sulphuric acid in the water-absorbing U tube.

be allowed to remain in the combustion tube until cold. When the boat is so far cooled that volatilization or decomposition of the substance is no longer to be feared, it is removed from the tube with a pair of tongs, placed on a sheet of thin copper foil, and by means of the polished iron hook (fig. 70) a portion of the oxide of copper is transferred to the small brass shovel (fig. 71). The substance is now quickly distributed over the oxide of copper left in the boat, covered with the oxide in the shovel, the boat at once returned to the combustion tube, with which the absorption apparatus has been previously connected, the hinder end of the tube is closed with its cork, and air passed slowly through the apparatus. The combustion is conducted as usual, the substance is heated, beginning in front and proceeding towards the back, whilst the middle and fore part of the tube are kept red hot. A comparison of the air-bubbles passing through the potash bottle of the air-purifying apparatus on the one side, and the weighed potash bulbs on the other side, will enable the operator to see how the process is going on and when it is finished. Finally, the weighed absorption apparatus is removed, the heating of the tube being continued whilst a powerful stream of air is passed through it to reoxidize the reduced copper; it is then ready for the next analysis.

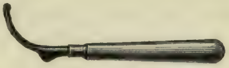
Fig. 70.

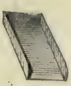
Fig. 71.

Liquid non-volatile substances are treated in the same way, being transferred to the oxide of copper in the boat *C E* by the aid of a drawn-out tube, and their weight is ascertained by reweighing the tube. Volatile hydrocarbons (amylene, benzene, &c.) are weighed in a small stoppered tube with a drawn-out end. The stopper being removed, the tube is laid on the oxide of copper in the boat *C E*, at the end, the boat is put back into the combustion tube, and a slow stream of air is passed through the tube, the foremost half of which is red hot. If the stream of air is not sufficient to convey the liquid to the oxide of copper at the ordinary temperature, the part of the tube containing the liquid must be heated, proceeding from front to back.

In the combustion of nitrogenous substances, the boat *D*, usually filled with oxide of copper, is replaced by a copper boat filled with copper turnings, whose surface has been first oxidized, and then reduced by ignition in a stream of hydrogen. The current of air must be particularly slow in the first part of the operation, and somewhat more rapid towards the close, in order that the fore part of the boat may remain metallic to the end, so as to be capable of reducing the oxides of nitrogen.

In the analysis of substances containing sulphur, chlorine, bromine or iodine, the boat *C E* is filled with chromate of lead, and the boat *D* with perfectly dry red lead or chromate of lead, the foremost boat being heated merely to incipient redness, that its contents may not fuse.

Carbon compounds, containing inorganic bodies, are placed in a porcelain boat, and this is pushed up to the permanent layer of oxide of copper in the middle of the tube on a piece of platinum foil with turned-up

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This explains the circumstance that Cloëz always found a few tenths per cent. too much hydrogen. The sulphuric acid tube in the drying apparatus should come next the combustion tube.

edges by means of a wire fastened to the foil. When the products of dry distillation have been consumed, the residual carbon is finally burnt at the expense of the oxygen of the stream of air. In the case of very difficultly combustible substances—such as the graphite-like carbon deposited in gas retorts—the operation takes a somewhat longer time than when oxygen is employed; but, according to CLOEZ, the results are equally accurate.

The apparatus is also described as being applicable to the estimation of *nitrogen* by volume, on DUMAS' principle (§ 185, *aa*). The foremost boat is then filled with copper turnings which have been oxidized and afterwards reduced; the hinder boat with oxide of copper and the substance. Pure carbonic acid is led into the hinder end of the tube by means of a tube provided with a stopcock, until all the air is expelled, the cock is then turned off, the point of the gas delivery tube attached to the front of the tube is put under the cylinder filled with mercury and potash solution, and the tube, which has previously been brought to redness in the middle and in front, is now heated behind; finally the cylinder is raised as high as practicable in order to diminish as much as possible the pressure of the mercury, and the cock being opened, carbonic acid is passed through the tube until the whole of the nitrogen is transferred to the cylinder; the other details of the process will be found in § 185, *aa*. In constructing the carbonic acid apparatus, it must be remembered that the gas will have to overcome the pressure of the mercury.

b. C. M. WARREN, whose methods for estimating sulphur and chlorine have been already described, § 188, 5, *a*, and § 190, 3, also burns solely or almost solely at the expense of oxygen, in estimating carbon and hydrogen. The hinder part of his combustion tube is bent upwards at an obtuse angle. The substance is placed in the inclined portion of the tube, into which oxygen or air is passed as required, and is heated by a special gas-lamp—for volatile bodies, a copper rod is placed between. The horizontal part of the tube contains, next the bend, 30—36 cm. of asbestos very uniformly packed, then 6—9 cm. strongly ignited coarse oxide of copper, and lastly, a plug of asbestos. The oxide of copper serves as an indicator to show whether any unburnt gases penetrate as far as it and to complete their combustion if necessary.

c. There are three other methods, for the details of which reference must be made to the original papers, viz., WHEELER'S,* for estimating carbon, hydrogen, and nitrogen in one analysis, FRANZ SCHULZE'S,† which depends on gas-measuring and also admits of the nitrogen being determined, and T. SCHLÖSING'S‡ for estimating carbon, hydrogen, and oxygen in one analysis.

d. BRUNNER§ oxidizes the substance in the wet way, with dichromate of potassa and sulphuric acid. This process has been modified by ULLGREN, who uses a mixture of chromic acid with sulphuric acid, and is used for estimating carbon in iron (see "Analysis of Cast Iron").

III. DETERMINATION OF THE EQUIVALENT OF ORGANIC COMPOUNDS.

The methods of determining the equivalent of organic compounds differ essentially according to the properties of the various compounds. There are three general methods in use for this purpose.

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* Jour. f. prakt. Chem. 96, 239; Zeitschr. f. anal. Chem. 5, 217.

† Zeitschr. f. anal. Chem. 5, 269.

‡ Compt. rend. 65, 957; Zeitschr. f. anal. Chem. 7, 270.

§ Pogg. Annal. 95, 379; Jahresb. v. LIEBIG u. KOPP, 1855, 773.

§ 193.

1. *An estimation is made of the amount of a Body of known Equivalent, which combines with the substance whose Equivalent is to be determined, to form a well-characterized Compound.*

In this way, the equivalent of organic acids and bases is determined, and also that of many indifferent bodies which have the property of combining with bases or acids. The mode of calculating the equivalent from the results obtained will be found under "The Calculation of Analyses." The methods only will be given here.

a. The equivalent of *organic acids,* in most cases, is determined from the silver salt, because the analysis is very simple, and there is almost always the positive certainty that the analysed salt is not a basic or hydrated compound. Other salts, however, are also frequently used, particularly those of lead, baryta, and lime. (In the analysis of lead salts, care must be taken not to mistake basic for neutral salts: and in the analysis of baryta and lime salts, hydrated must not be taken for anhydrous salts.) The manner in which the determination of the bases in question is effected, is fully described in Section 4 (Vol. I.).

b. The equivalent of *organic bases* which form well-crystallized salts with sulphuric, hydrochloric, or any other easily determined acid, is best ascertained by estimating the amount of acid contained in a weighed quantity of the salt, by the usual methods.

If the salts do not crystallize, a weighed quantity of the dry alkaloïd is, according to Liebig, introduced into a drying tube (fig. 72), which is then accurately weighed with its contents, and a current of dry hydrochloric acid gas is passed slowly through the apparatus for some time; the tube being ultimately heated at 100° (see § 29, vol. I. fig. 34), and a stream of atmospheric air passed through it; the quantity of hydrochloric acid absorbed is found from the increase in the weight of the tube. The accuracy of the results may be controlled by dissolving the hydrochloride in water, and precipitating the chlorine by nitrate of silver. The equivalent of the alkaloïds may be determined also from the insoluble double salts produced by precipitating the solution of their hydrochlorides with bichloride of platinum; the platinochlorides are then carefully ignited (§ 124), and the residuary platinum weighed.

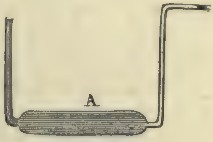

Fig. 72.

c. In the case of *indifferent bodies,* there is usually no choice about the matter, and we have to determine the equivalent from the lead compound; since many of these substances either do not form compounds with bases other than oxide of lead, or form compounds which cannot be obtained in a state of purity. Although in this way the matter is left in doubt, as the oxide of lead often combines with such substances in varying proportions, yet the analysis of such compounds is always of interest, as it shows whether the substance combines with the oxide of lead directly, or with elimination of water.

Sometimes organic substances yield solid and crystallizable compounds with water, by the analysis of which their equivalents may be determined.

§ 194.

2. *The Vapour Density of the Compound is determined.*

Of the numerous methods which have been proposed with this object, the two which are more frequently employed in laboratories as the simplest and most suitable are here described in detail. In all determinations of vapour densities, it is necessary that the temperature at which they are made should be sufficiently raised above the boiling point of the substances, so that the vapour may have the coefficient of expansion of a gas. The extreme importance of this rule is evident from the fact that at temperatures only slightly above the boiling point the density vapour found is too high, the density decreasing with the increase of temperature, and becoming constant only after a certain point.

A. DUMAS' PROCESS.

The following are the outlines of this method:—A light glass globe, filled with dry air, and the exact capacity of which is afterwards ascertained, is accurately weighed; the weight of the air in the globe is calculated for the temperature and pressure observed during the process of weighing, and the result subtracted from the first weight: the difference expresses the weight of the vessel when empty of air. The substance, the vapour density of which it is intended to determine, is then introduced into the globe in more than sufficient quantity, and exposed to a uniform temperature sufficiently above the boiling point of the substance, until it is completely converted into vapour, and the excess expelled, together with the atmospheric air originally contained in the globe; the vessel is then sealed and weighed. The difference between the weight found and that of the empty globe, is the weight of a given volume of the vapour; this supplies the necessary data for calculating its specific gravity. It is hardly necessary to remark that the volume of the air and the vapour must be reduced to the same pressure and temperature, and consequently that the state of the barometer and thermometer must be noted both during the first weighing and at the time of sealing the glass globe.

This method is of course applicable only to substances which volatilize without decomposition; moreover, to obtain accurate results, it is indispensable that the substance should be perfectly pure. The practical working of the process will be described here, whilst the necessary corrections and the calculation of the results, as well as their bearing on the composition of the substance, will be considered in the "Calculation of Analysis," § 204.

a. Apparatus and other Requisites.

1. THE SUBSTANCE.—About 8 grams are required. The boiling point must be pretty accurately known.

2. A GLASS GLOBE WITH DRAWN-OUT NECK.—An ordinary globe of pure glass is selected, free from flaws, and holding from 250 to 500 c. c.; it is carefully rinsed with water, and then thoroughly dried. After

this, it is completely exhausted, dry air is readmitted into it, and the same operation repeated, the apparatus illustrated in fig. 24, § 174, being used for this purpose. The neck of the globe is then softened near the body, and drawn out in the shape represented in fig. 73.

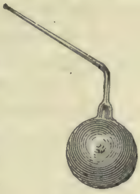
Fig. 73.

The extreme point is cut off and the edges slightly rounded over the lamp. (This point having to be sealed air-tight with the greatest despatch, at a subsequent stage of the process, it is advisable to ascertain, in the first place, whether the glass of the globe is readily fusible or not; this may be done by trying to seal the point on the original neck of the globe; should this present any difficulty, the globe is unfit for the intended purpose.)

3. A SMALL IRON or COPPER VESSEL for the reception of the liquid in which the globe is to be heated (see fig. 74). The liquid which is to serve for the bath must admit of being heated to at least 30° or 40° beyond the boiling point of the substance. Water, paraffin, or oil will answer the purpose in nearly all cases. A chloride of calcium bath, however, is more convenient than a paraffin or oil bath, if its temperature (which in a perfectly saturated bath may be raised to 180°) is sufficiently high for the purpose, as the globe may be more easily cleaned.

4. AN APPARATUS TO KEEP THE GLOBE IN POSITION —This may be readily made with a rod and some iron wire. During the operation, it is attached to a retort-stand (see fig. 74).

5. A quantity of MERCURY more than sufficient to fill the globe.

6. A GRADUATED TUBE of about 100 c. c. capacity.

7. A GAS- or SPIRIT-LAMP and BLOWPIPE.

8. An accurate BAROMETER.

9. An accurate THERMOMETER, with a sufficiently long scale.

b. The Process.

a. The globe is weighed, a thermometer being placed inside the case of the balance; the globe is left for ten minutes on the scale to ascertain whether its weight remains constant. If so, the weight is noted together with the height of the barometer, and the temperature indicated by the thermometer inside the case.

β. The globe is gently heated, and the point dipped down into about 8 grams of the substance, which, if solid, must be previously liquefied by the application of a gentle heat. (If the substance has a high melting point, the neck and point of the globe must be heated as well as the body, to guard against the fluid solidifying in the neck.) As the globe cools —which, in the case of very volatile substances, should be accelerated by dropping ether upon it—the fluid enters and spreads over it. Do not introduce more than 5—7 grams.

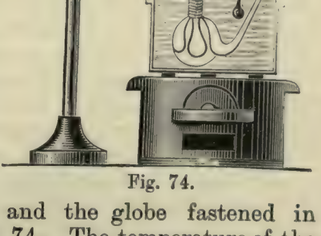
Fig. 74.

γ. The bath is heated to 40° or 50°, and the globe fastened in along with a thermometer, as shown in fig. 74. The temperature of the bath is now raised 30° to 40° above the boiling point of the substance, and (if a chloride of calcium, paraffin, or oil bath is used) the temperature towards the end of the operation must be maintained as uniform as possible by carefully regulating the heat. As soon as the temperature in the globe is somewhat higher than the boiling point of the substance, the vapour of the latter streams out through the orifice of the neck; the force of the current increases at first with the temperature of the bath, but diminishes afterwards by degrees, and finally (after about 15 minutes) ceases altogether. Should any of the vapour have condensed in drops in the point of the neck projecting from the bath, these may be at once converted into vapour by moving a piece of red-hot charcoal to and fro under it. The moment that a perfect equilibrium is fully established at the desired temperature, the point of the globe is quickly sealed by means of a blowpipe, and the height of the thermometer immediately noted. To be sure that the point is hermetically sealed, a current of air is directed on to the projecting point of the neck by the blowpipe; a small portion of the vapour will condense and form a column of fluid, which is retained in the end of the tube by capillary attraction; this will not take place if the tube is not hermetically sealed. The height of the barometer also is noted again, to see if it has changed since the first observation.

δ. The sealed globe is now taken out of the bath, allowed to cool, cleaned most carefully, completely dried, and weighed again in the same manner as before.

ε. The pointed end of the globe is immersed in mercury in its entire length, a file-mark is made near the end, and the point broken off; the mercury at once rushes into the globe, a vacuum having been created in it by the condensation of the vapour. (In this operation, the glass globe should be placed in the hollow of the hand, which rests upon the edge of the mercurial trough.) If the globe, at the moment it was sealed, was quite free from air, it will be completely filled with mercury; otherwise an air-bubble will remain in it. In either case the mercury in the globe is transferred to the graduated tube and accurately measured; if there was a bubble of air, the globe is now filled with water, and this also is measured: the difference between the volume of the mercury and that of the water shows the volume of the air which had remained in the globe.

For the calculation see § 204.

B. Process based on Gay-Lussac's Principle.

Whilst in Dumas' process a quantity of vapour of known volume under determined conditions is cooled and weighed, in Gay-Lussac's process a quantity of substance of known weight is converted into vapour and this is measured under determined conditions. The latter process is best carried out in the manner recommended by A. W. Hofmann.*

For this purpose, a calibrated glass tube is required, closed at one end and about a metre long and 15 to 20 mm. wide. This tube is carefully filled with mercury and inverted in a small mercurial trough, so that a vacuum of 20 to 30 cm. is formed at the top. Almost the entire length of the tube is surrounded by another glass tube, 80 to 90 cm. long and 30 to 40 mm. wide, which is narrowed at the top—over the sealed end of the calibrated tube—to a smaller tube bent at right angles. The external tube is closed below with a cork, through the middle of which the calibrated tube passes; whilst a second tube is also fitted into another perforation of the cork.

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* Ber. d. deutsch. chem. Gesellsch. 1, 198; Zeitschr. f. anal. Chem. 8, 83.

The external tube serves the purpose of raising the inner tube to a definite high temperature and to maintain it thereat by passing the vapour of a liquid of constant and suitable boiling point (water, aniline, &c.) through the upper bent tube bent at right angles. If water is used, the steam is allowed to escape from the small tube below; if aniline or some other liquid is used the small tube is connected with a condenser. Hofmann has satisfied himself by direct experiment, that, if the evolution of vapour is rapid enough, the temperature of the calibrated tube will remain without change at the boiling point of the liquid used; this renders it unnecessary to take the temperature during the experiment.

The liquid, whose vapour-density is to be estimated, is weighed in a very small bottle, made from a piece of thin glass tubing and closed with a ground glass stopper. The capacity of the flask depends on the nature of the liquid, and varies from 10 to 100 mgrm. of water. The weighed flask is allowed to rise in the calibrated barometer tube. The stopper usually springs out as soon as the flask reaches the barometric vacuum; but whether this takes place or not, heat is at once applied by passing in the vapour of water, or aniline, or other liquid of constant boiling point through the upper tube from a glass or copper vessel in which the liquid is boiled. After a short time, when the stopper has been expelled from the little bottle, the liquid flows out and becomes vaporized, the column of mercury in the calibrated tube sinking at the same time. When the hot vapour has circulated in the space between the two tubes for some time, so that the temperature may be taken as constant and the height of the mercury column does not change, the height of the barometer and that of the mercury, within and without the calibrated tube, are read off; the latter should have a millimetre graduation as well as the c. c. graduation. The temperature both of the vapour and the quicksilver is that of the boiling point of the liquid used for heating at the observed barometric pressure. The calculation is explained in § 204. If a high temperature is used, the tension of mercurial vapour and the temperature of the mercury must be taken into account. As to the latter point, a trifling error cannot be avoided, as the mean temperature of the mercury at the spot where the heated metal joins the unheated cannot be ascertained; this however has no appreciable influence on the result.

Hofmann's process offers important advantages, as it makes it possible to use Gay-Lussac's principle for the determination of vapour-densities at high temperatures, without being troubled in any way by the poisonous fumes of mercury; the atmosphere of vapour gives a constancy of temperature otherwise difficult to obtain; and the volume of the vapour may be read off with the greatest accuracy. The greatest advantage however is that at so low a pressure, which may be diminished to 20 or even 10 cm., one can work at a comparatively low temperature. For many bodies, with boiling points as high as 120° and even 150° (according to A. Schröder, 182°) steam is sufficient; and the vapour of boiling aniline, which boils at 185°, under these conditions is hot enough not only for taking its own density, but also for that of toluidine boiling at 198° and naphthaline boiling at 218°, and, according to SCHRÖDER, even for coumarine, which boils at 270°.*

H. WICHELHAUS† recommends the modification of HOFMANN's apparatus shown in fig. 75. *a* is a ground glass cup which fits the orifice of the internal calibrated tube, and is put on in the mercurial trough, after the substance has been introduced. It remains, full of mercury, joined to the graduated tube, forming a syphon, and thus allowing the tube to be entirely surrounded by the heated vapour, and the operation to be completed without further use of a trough. The difficulty previously alluded to regarding the variation in temperature of different parts of the mercurial column is thus entirely obviated.

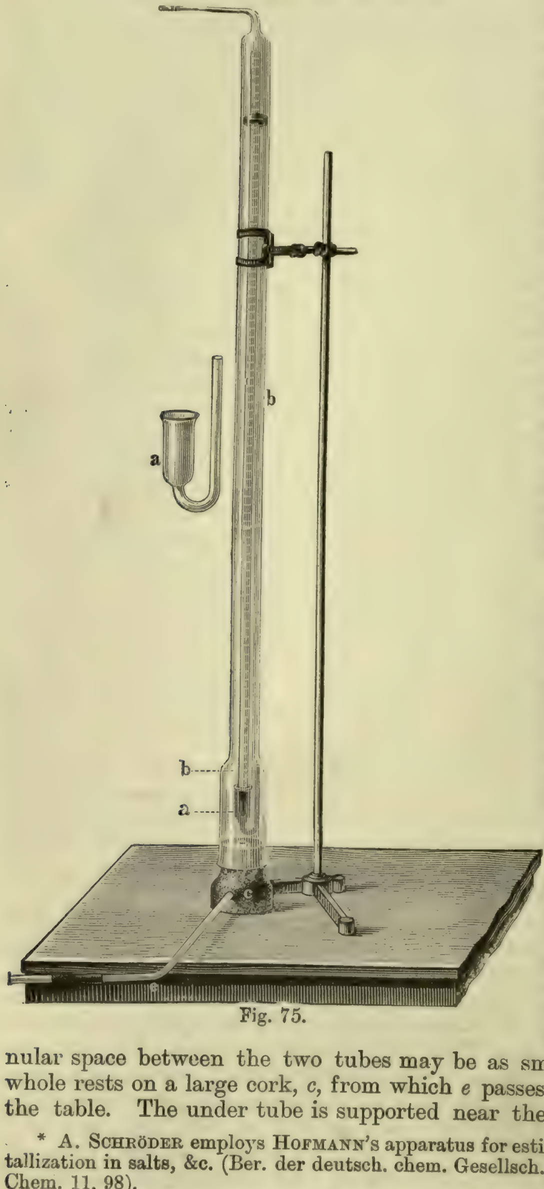

Fig. 75.

The mercury driven out when the tube is heated flows out through the narrow orifice of the glass cup, and then through *e*, along with the vapour, into the condenser and receiver. The line *b* is the zero-point on the tube which is divided into cubic centimetres and millimetres and from which the height is always read off. The outer tube *d* is widened to the necessary extent below, so that the annular space between the two tubes may be as small as possible. The whole rests on a large cork, *c*, from which *e* passes above the surface of the table. The under tube is supported near the top by a cork with notches cut in the outside to allow the vapour to pass, as if it were allowed to rest on the syphon cup the latter would be broken by the weight.

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* A. SCHRÖDER employs HOFMANN's apparatus for estimating the water of crystallization in salts, &c. (Ber. der deutsch. chem. Gesellsch. 4, 471; Zeitschr. f. anal. Chem. 11, 98).

† Ber. der deutsch. chem. Gesellsch. 1870, 166; Zeitschr. f. anal. Chem. 9, 496.

Other methods, based on GAY-LUSSAC'S principle, have also been proposed by HUGO SCHIFF,* and W. M. WATTS,† and others.

C. GRABOWSKI'S‡ and LANDOLT'S§ methods are founded on a slightly different principle from GAY-LUSSAC'S. In GRABOWSKI'S process, two similar tubes, at first filled with mercury, are heated to the same temperature in an air bath. One of these tubes receives the bulb or little bottle containing the weighed substance. As soon as the vapour of the fluid has reached the necessary temperature, dry air is passed into the other tube until the volume of air is the same as that of the vapour. This equality must continue on increasing the temperature (unless dissociation takes place), and also on cooling to the temperature which is the lower limit of the normal vapour density of the substance. When quite cold, the quantity of air used is measured in the usual way, and the vapour density of the substance calculated from it.

Whilst in GRABOWSKI'S method the quantity of the normal substance (air) is adapted to that of the substance to be examined, LANDOLT, on the contrary, adapts the weight of the substance to be examined to that of the normal substance (water or chloroform). The direct equalizing of the volumes at the same pressure and temperature is common to both processes. L. PFAUNDLER,‖ who has made a critical examination of both methods, proposes a modification of GRABOWSKI'S apparatus, in which the tubes are heated by a vapour, and the air is admitted in a different way.

D. BUNSEN'S method¶ is based on the well-known principle that the specific gravity of gases and vapours is known if the weight of equal volumes under the same conditions is known; but the application of it is entirely original. Three, or perhaps two, glass tubes are required, similar in their capacity to the hundredth of a c. c., and in their weight to the fraction of a mgrm. BUNSEN employs an air-tight stopper of such simple construction that it is possible to use the same tubes, weighed once for all, in estimating the density of gases and vapours, as many times as you like. For heating them, he uses a large air bath of peculiar construction, which allows the temperature to be maintained nearly constant for a long time.

The speciality of the process (which is accurately described in detail) consists in this: that the density of gases and vapours is obtained by always using the same tubes, and simply determining two different weights, without its being necessary to ascertain the volume, pressure, or temperature of the vapours. The accuracy of BUNSEN'S results is so great, that in the case of carbonic acid and ether vapour the numbers are identical to the third place of decimals, but the method requires a high degree of skill, and great practice in the construction of glass apparatus.

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* Zeitschr. f. anal. Chem. 1, 321.

† *Ibid.* 7, 82.

‡ *Ibid.* 5, 338.

§ *Ibid.* 11, 322.

‖ Ber. der deutsch. chem. Gesellsch. 5, 575; Zeitschr. f. anal. Chem. 12, 100.

¶ Zeitschr. f. anal. Chem. 6, 1.

E. For bodies of very high boiling point, Deville and Troost's* method is used, for a description of which the original paper must be consulted.

§ 195.

3. A great many indifferent organic bodies unfortunately do not combine with bases or acids; or only form compounds with them, from which the equivalent cannot well be determined. In such cases, the equivalent is determined by acting with acids, bases, halogens, &c., on the substance, so as to prepare substitution or other decomposition products, the equivalents of which are known or can be ascertained, or it may be inferred from the mode of formation of the compound in question. In these cases, that equivalent is assumed to be the correct one which affords the simplest explanation of the processes of formation and decomposition.

This mode of determining the equivalent of substances is intimately connected with the higher branches of organic chemistry, and cannot be considered in detail here, as it is impossible to give methods which are universally applicable.

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* Annal. d. Chem. u. Pharm. 113, 42.

DIVISION II.

CALCULATION OF ANALYSES.

The calculation of the results obtained by an analysis presupposes, as an indispensable preliminary, a knowledge of the general laws of the combining proportions of bodies, on the one hand, and of the more simple rules of arithmetic on the other. It is a great error to suppose that it is necessary to be a good mathematician in order to make chemical calculation; a knowledge of decimal fractions and simple equations being sufficient for the most part. These remarks are not intended to dissuade students of chemistry from pursuing the highly important study of mathematics; but merely to encourage those who have had no opportunity of entering more deeply into this science, and who, as the author knows from experience, are often afraid to venture upon chemical calculations. For this reason, the whole of the calculations given in the following paragraphs, are made in the most intelligible manner possible, and without using logarithms.

I. *Calculation of the Constituent sought from the Compound obtained in the Analytical Process, and conversion of the Result in Per-cents.*

§ 196.

The bodies, the weight of which it is intended to determine, are separated, as we have seen in Division I., treating of the "Execution of Analysis," either in the free state, or—and this most frequently—in combinations of known composition. The results are usually calculated on 100 parts of the substance examined, as this gives a clearer view of the composition. In cases where the several constituents have been separated in the free state, the calculation may be made directly; but if the constituents have been separated in combination with other substances, they must first be calculated from the compounds obtained.

1. *Calculation of the Results into Per-cents by Weight, when the Substance sought has been separated in the Free State.*

a. Solid Bodies, Liquids, and Gases, which have been determined by Weight.

§ 197.

The calculation here is exceedingly simple.

Suppose mercurous chloride to have been analysed, and the mercury separated in the metallic state (§ 118, 1, Vol. I.) 2·945 grams mercurous chloride have given say 2·499 grams mercury.

$$2{\cdot}945 : 2{\cdot}499 :: 100 : x \qquad \therefore x = 84{\cdot}85,$$

which means that the analysis shows 100 parts of mercurous chloride to contain 84·85 of mercury, and consequently 15·15 of chlorine.

Now as the mercurous chloride is known to consist of 2 eq. mercury and 1 eq. chlorine, and as the equivalent numbers of both these elements are also known, the true percentage composition may be readily calculated from these data. When analysing substances of known composition for practice, the results theoretically calculated and those obtained by the analysis are usually placed in juxtaposition, as this enables the student at once to perceive the degree of accuracy with which the analysis has been performed. Thus for instance—

	Found.	Calculated (compare § 84, *b*, Vol. I.)
Mercury . . .	84·85	84·94
Chlorine . . .	15·15	15·06
	100·00	100·00

b. Gases which have been determined by Measure.

§ 198.

If a gas has been determined by measure, it is, of course, necessary first to ascertain the weight corresponding with the volume found, before the percentage by weight can be calculated. But as the exact weights of a definite volume of the various gases have been severally determined by accurate experiments, this calculation also is a simple rule-of-three question, if the gas can be measured under the same circumstances as those under which the known relation of weight to volume was determined. The circumstances to be taken into consideration, are:

Temperature and Atmospheric Pressure.

Besides these, the

Tension of the Aqueous Vapour.

may also have to be considered in cases where water is used as the confining fluid, or generally where the gas has been measured in the moist state.

The respective weights assigned in Table V.* to 1 litre of the gases there enumerated, refer to a temperature of 0°, and an atmospheric pressure of 760 millimetres of mercury. We have, therefore, in the first place, to consider the manner in which volumes of gas measured at another temperature and another height of the barometer, are to be reduced to 0° and 760 mm. of the barometer.

a. Reduction of a Volume of Gas of any given Temperature to 0°, *or any other Temperature between* 0° *and* 100°.

The following propositions regarding the expansion of gases were formerly universally adopted:—

1. All gases expend alike for an equal increase of temperature.
2. The expansion of one and the same gas for each degree of the thermometer is independent of its original density.

Although the correctness of these propositions has not been fully confirmed by the accurate investigations of MAGNUS and REGNAULT, yet they may be safely followed in reductions of the temperature of those gases which are most frequently measured in the course of analytical processes, as the coefficients of expansion of these gases scarcely differ from each other, and as there is never any very considerable difference in the pressure under which the gases are severally measured.

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* See Tables at the end of the volume.

The investigations just alluded to have given

$$0{\cdot}3665$$

as the coefficient of the expansion of gases which comes nearest to the truth; in other words, as the extent to which gases expand when heated from the freezing to the boiling point of water. They expand, therefore, for every degree of the centigrade thermometer,

$$\frac{0{\cdot}3665}{100} = 0{\cdot}003665.$$

If we wish to ascertain how much space 1 c. c. of gas at 0° will occupy at 10°, we find

$$1 \times (1 + 10 \times 0{\cdot}003665) = 1{\cdot}03665.$$

If we wish to ascertain how much space 100 c. c. at 0° will occupy at 10°, we find

$$100 \times (1 + 10 \times 0{\cdot}003665) = 100 \times 1{\cdot}03665 = 103{\cdot}665.$$

If we wish to know how much space 1 c. c. at 10° will occupy at 0°, we find

$$\frac{1}{1 + 10 \times 0{\cdot}003665} = 0{\cdot}965.$$

How much space do 103·665 c. c. at 10° occupy at 0°?

$$\frac{103{\cdot}665}{1 + 10 \times 0{\cdot}003665} = 100.$$

The general rule of these calculations may be expressed as follows:—

To calculate the volume of a gas from a lower to a higher temperature, we have in the first place to find the expansion for the volume unit, which is done by adding to 1 the product of the multiplication of the thermometrical difference by 0·003665; and then to multiply this by the number of volume units found in the analytical process. On the other hand, to reduce the volume of a gas from a higher to a lower temperature, we have to divide the number of volume units found in the analytical process, by 1 + the product of the multiplication of the thermometrical difference by 0·003665.

In the case of carbonic acid, the coefficient of expansion differs somewhat from that of air and other permanent gases. According to MAGNUS it is 0·00369 for 1° C., according to REGNAULT 0·00371.

β. *Reduction of the Volume of a Gas of a certain given density to* 760 *millimetres Barometric Pressure, or any other given Pressure.*

According to MARIOTTE's law (which applies to most gases and pressures usually occurring in gas analyses) the volume of a gas is inversely as the pressure to which it is exposed; in accordance with this, a gas occupies the greater space the less the pressure upon it, and the less space the greater the pressure upon it.

Thus, supposing a gas to occupy a space of 10 c. c. at a pressure of 1 atmosphere, it will occupy 1 c. c. at a pressure of 10 atmospheres, and 100 c. c. at a pressure of $\frac{1}{10}$ atmosphere.

Nothing, therefore, can be more easy than the reduction of a gas of a certain given tension to the normal barometric pressure of 760 mm., or to any other given pressure, such as 1,000 mm., which is frequently used in the analysis of gases.

Supposing a gas to occupy 100 c. c. at 780 mm. bar., how much space will it occupy at 760 mm.?

$760 : 780 :: 100 : x \qquad \therefore x = 102{\cdot}63.$

How much space will 100 c. c. at 750 mm. bar. occupy at 760 mm.?

$760 : 750 :: 100 : x \qquad \therefore x = 98{\cdot}68.$

How much space will 150 c. c. at 760 mm. bar. occupy at 1000 mm.

$1000 : 760 :: 150 : x \qquad \therefore x = 114.$

Condensible gases do not exactly follow MARIOTTE's law, those which are most readily condensible deviating most. Of such gases, carbonic acid is that which is most commonly met with in these analyses, but the differences of pressure under which it is measured are so slight that the error involved need not be taken into account, unless the very highest degree of accuracy is required. For large differences of pressure the deviation from the law becomes more marked; for instance, to condense carbonic acid to half its volume (at the same temperature), a pressure of 1·98292 (REGNAULT) instead of two atmospheres will be required.

γ. Reduction of the Volume of a Gas saturated with Aqueous Vapour, to its actual Volume in the Dry State.

It is a well-known fact that water has a tendency, at all temperatures, to assume the gaseous state. The degree of this tendency (the tension of the aqueous vapour)—which depends solely and exclusively on the temperature, and not on the circumstance of the water being in a vacuum or in any gaseous atmosphere—is usually expressed by the height of a column of mercury capable of counterbalancing it. The following table gives this tension for the various temperatures at which analyses are likely to be made[*] :—

TABLE.

Temperature (in degrees C.)	Tension of the aqueous vapour expressed in millimetres.	Temperature (in degrees C.)	Tension of the aqueous vapour expressed in millimetres.
0	4·525	21	18·505
1	4·867	22	19·675
2	5·231	23	20·909
3	5·619	24	22·211
4	6·032	25	23·582
5	6·471	26	25·026
6	6·939	27	26·547
7	7·436	28	28·148
8	7·964	29	29·832
9	8·525	30	31·602
10	9·126	31	33·464
11	9·751	32	35·419
12	10·421	33	37·473
13	11·130	34	39·630
14	11·882	35	41·893
15	12·677	36	44·268
16	13·519	37	46·758
17	14·409	38	49·368
18	15·351	39	52·103
19	16·345	40	54·969
20	17·396		

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[*] Compare MAGNUS, Pogg. Annal. 61, 247.

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Therefore, if a gas is confined over water, its volume is, *cæteris paribus*, always greater than if it were confined over mercury; since a quantity of aqueous vapour, proportional to the temperature of the water, mixes with the gas, and the tension of this partly counterbalances the column of air that presses upon the gas, and to that extent neutralizes the pressure. To ascertain the actual pressure upon the gas, therefore, we must subtract from the apparent pressure so much as is neutralized by the tension of the aqueous vapour.

Suppose we have found a gas to measure 100 c. c. at 759 mm. bar., the temperature of the confining water being 15°; how much space would this volume of gas occupy in the dry state and at 760 mm. of the barometer?

According to the table, the tension of aqueous vapour at 15° = 12·677; the gas is consequently not under the apparent pressure of 759 mm., but under the actual pressure of $759 - 12{\cdot}677 = 746{\cdot}323$ mm.

The calculation is now very simple; it proceeds in the manner shown in β; we say,

$$760 : 746{\cdot}323 :: 100 : x \qquad \therefore x = 98{\cdot}2.$$

When the volume of a gas has thus been reduced by the calculations shown in α and β, or γ, to the thermometrical and barometrical conditions to which the data of Table V. refer, the percentage by weight may be readily calculated by substituting the weight for the volume, and proceeding by simple rule of three.

What is the percentage by weight of nitrogen in an analysed substance, of which ·5 gram has yielded 30 c. c. of dry nitrogen gas at 0°, and 760 mm. bar.?

In Table V. we find that 1 litre (1000 c. c.) of nitrogen gas at 0°, and 760 mm. bar., weighs 1·25617 gram:—We say accordingly:

$$1000 : 1{\cdot}25617 :: 30 : x \qquad \therefore x = 0{\cdot}0377.$$

And then:

$$0{\cdot}5 : 0{\cdot}0377 :: 100 : x \qquad \therefore x = 7{\cdot}54.$$

The analysed substance contains consequently 7·54 per cent. by weight of nitrogen.

2. *Calculation of the Results into Per-cents by weight, in Cases where the Body sought has been separated in Combination, or where a Compound has to be determined from one of its Constituents.*

§ 199.

If the body to be determined has not been weighed or measured as such, but in some other form, for example, carbonic acid as carbonate of lime, sulphur as sulphate of baryta, ammonia as nitrogen, chlorine by a standardised solution of iodine, &c., its quantity must first be reckoned from that of the compound found, before the calculation described in 1 can be made. This may be accomplished either by rule of three or by some abridged method.

Suppose we have weighed hydrogen in the form of water, and have found 1 gram of water; how much hydrogen does this contain?

An equivalent of water consists of:

$$\begin{array}{l} 1 \text{ part of hydrogen by weight} \\ \underline{8} \text{ parts of oxygen by weight} \\ 9 \text{ parts of water by weight.} \end{array}$$

We say accordingly:

$$9 : 1 :: 1 : x \qquad \therefore x = 0{\cdot}11111.$$

The above proportion gives the equation:

$$\frac{1}{9} \times 1 = x, \text{ or } 0{\cdot}11111 \times 1 = x.$$

Or, expressed in general terms:

Water × 0·11111 = *Hydrogen.*

EXAMPLE.—

517 of water; how much hydrogen?
517 × 0·11111 = 57·444.

The following equation also is derived from the above proportion:

$$\frac{9}{1} = \frac{1}{x} \therefore 9 = \frac{1}{x} \text{ or } x = \frac{1}{9}.$$

Or, expressed in general terms,

Water divided by 9 = *Hydrogen.*

EXAMPLE.—

517 of water, how much hydrogen?

$$\frac{517}{9} = 57{\cdot}444.$$

In this manner, for every compound, constant numbers may be found by which to multiply or divide the weight of the compound, in order to find the weight of the constituent sought (comp. Table III.*).

Thus, for instance, the nitrogen may be obtained from the platinochloride of ammonium, by dividing the weight of the latter by 15·884, or multiplying it by 0·602957; and the carbon may be calculated from the carbonic acid by multiplying the weight of the latter by 0·2727, or dividing it by 3·666.

These numbers are by no means so simple, convenient, and easy to remember as in the case of hydrogen. It is therefore advisable, in the case of carbonic acid, for instance, to fix upon another general expression, viz.,

$$\frac{\textit{Carbonic acid} \times 3}{11} = \textit{Carbon};$$

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* See Tables at the end of the volume.

which is derived from the proportion

22 : 6 :: the carbonic acid found : x.

The object in view may also be attained in a very simple manner, by means of Table IV.,* which gives the amount of the constituent sought for every number of the compound found, from 1 to 9; the operator need, therefore, simply add the several values together.

With hydrogen, for instance, we find :—

TABLE.

Found.	Sought.	1	2	3	4	5	6	7	8	9
water	hydrogen	0·11111	0·22222	0·33333	0·44444	0·55555	0·66667	0·77778	0·88889	1·00000

From this table it is seen that 1 part of water contains 0·11111 of hydrogen, that 5 parts of water contain 0·55555 of hydrogen; 9 parts, 1·00000, &c.

Now, if it is wished to know, for instance, how much hydrogen is contained in 5·17 parts of water, this may be found by adding the values for 5 parts, for $\frac{1}{10}$ part, and for $\frac{7}{100}$ parts, thus :—

$$\begin{array}{l} 0{\cdot}55555 \\ 0{\cdot}011111 \\ 0{\cdot}0077778 \\ \hline 0{\cdot}5744388 \end{array}$$

Why the numbers are to be placed in this manner, and not as follows :—

$$\begin{array}{l} 0{\cdot}55555 \\ 0{\cdot}11111 \\ 0{\cdot}77778 \\ \hline 1{\cdot}44444 \end{array}$$

is self-evident, since arranging them in the latter way would be adding the value for 5, for 1, and for 7 ($5 + 1 + 7 = 13$) and not for 5·17. This consideration shows also that, to find the amount of hydrogen contained in 517 parts of water, the points must be transposed as follows :—

$$\begin{array}{r} 55{\cdot}555 \\ 1{\cdot}1111 \\ 0{\cdot}77778 \\ \hline 57{\cdot}44388 \end{array}$$

3. *Calculation of the Results of Indirect Analyses into Per-cents by Weight.*

§ 200.

The import of the term "indirect analysis," as defined on p. 405, Vol. I., shows sufficiently that no universally applicable rules can be laid down for the calculations which have to be made in indirect analyses. The selection of the right way must be left in each special case to the intelligence of the analyst. The mode of calculating the results in the more important indirect separations described in Section V. is given here. They may serve as examples for other similar calculations.

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* See Tables at the end of the volume.

a. Indirect Determination of Soda and Potassa.

This is effected by determining the sum total of the chlorides, and the chlorine contained in them.

The mode of calculation will be evident from the following example:—

Suppose 3 grams of chloride of sodium and chloride of potassium have been found, and 1·6876 of chlorine in these 3 grams.

E q. Chlorine.		Eq. KCl.		Chlorine found.			
35·46	:	74·59	::	1·6876	:	x	$\therefore x = 3{\cdot}55$.

If all the chlorine present were combined with potassium, the weight of the chloride would amount to 3·55. As the chloride weighs less, chloride of sodium is present, and this in a quantity proportional to the difference (*i.e.*, $3{\cdot}55 - 3 = 0{\cdot}55$), which is calculated as follows:—

The difference between the equivalent of KCl and that of NaCl (16·09) is to the equivalent of NaCl (58·50), as the difference found is to the chloride of sodium present:—

$$\therefore \quad 16{\cdot}09 : 58{\cdot}50 :: 0{\cdot}55 : x$$
$$\therefore x = 2\text{NaCl}$$
$$\text{and } 3 - 2 = 1\text{KCl}.$$

From this the following short rule is derived:—

Multiply the quantity of chlorine in the mixture by 2·1035, deduct from the product the sum of the chlorides, and multiply the remainder by 3·6358; the product expresses the quantity of chloride of sodium contained in the mixed chlorides.

The following formulæ* may also be used:—

$$74{\cdot}594\,k + 58{\cdot}5\,n = C \text{ (Sum of the chlorides)}$$
$$35.457\,k + 35{\cdot}457\,n = c \text{ (Total chlorine).}$$

k is the number of equivalents of chloride of potassium (expressed in grams) contained in the chloride of potassium present in the substance, and therefore also the number of equivalents of potassium in the potassium present, or the number of equivalents of chlorine in the chlorine combined with potassium.

n stands for the similar value as regards sodium.

$\therefore$ $74{\cdot}594\,k$ = chloride of potassium present
$58{\cdot}500\,n$ = ,, sodium ,,
$35{\cdot}457\,k$ = chlorine combined with potassium
$35{\cdot}457\,n$ = ,, ,, ,, sodium.

Using C and c as above, we have

$$n = \frac{C - 74{\cdot}594\,k}{58{\cdot}5} = \frac{c - 35{\cdot}457\,k}{35{\cdot}457}$$

---

* KRETSCHY, Zeitschr. f. anal. Chem. 15, 44. An error of the pen in this paper has been here corrected.

$$\text{and} \therefore k = \frac{C - 1{\cdot}6499\, c}{16{\cdot}094}$$

The quantity of chloride of potassium required is therefore:—

$$KCl = 74{\cdot}594\, k = 4{\cdot}634895\, C - 7{\cdot}647048\, c.$$

b. Indirect Determination of Strontia and Lime.

This may be effected by determining the sum total of the carbonates, and the carbonic acid contained in them (§ 154, 8, Vol. I.). Suppose we have found 2 grams of mixed carbonate, and 0·7383 of carbonic acid in these 2 grams.

$$\overset{\text{Eq. } CO_2}{22} : \overset{\text{Eq. } SrO,CO_2}{73{\cdot}75} :: \overset{CO_2 \text{ found.}}{0{\cdot}7383} : x \qquad \therefore x = 2{\cdot}47498.$$

If, therefore, the whole of the carbonic acid were combined with strontia, the weight of the carbonate would be 2·47498 grams. The deficiency, = 0·47498 is proportional to the carbonate of lime present, which is calculated as follows:—

The difference between the equivalent of SrO,CO_2, and the equivalent of CaO,CO_2 (23·75) is to the equivalent of CaO,CO_2 (50), as the difference found is to the carbonate of lime contained in the mixed salt:—

$$23{\cdot}75 : 50 :: 0{\cdot}47498 : x \qquad \therefore x = 1.$$

The mixture, therefore, consists of 1 gram carbonate of lime and 1 gram carbonate of strontia.

From this the following short rule is derived:—

Multiply the carbonic acid found by 3·3523, deduct from the product the sum of the carbonates, and multiply the difference by 2·10526; the product expresses the amount of carbonate of lime.

c. Indirect Determination of Chlorine and Bromine (§ 169, 1, Vol. I.).

Let us suppose the mixture of chloride and bromide of silver to have weighed 2 grams, and the diminution of weight on passing of chlorine over it to be 0·1 gram. How much chlorine is there in the mixed salt, and how much bromine?

The decrease of weight here is simply the difference between the weight of the bromide of silver originally present, and that of the chloride of silver which has replaced it; if this is borne in mind, it is easy to understand the calculation which follows:—

The difference between the equivalents of bromide of silver and chloride of silver is to the equivalent of bromide of silver as the ascertained decrease of weight is to x, that is, to the bromide of silver originally present in the mixture:—

$$44{\cdot}49 : 187{\cdot}88 :: 0{\cdot}1 : x \qquad \therefore x = 0{\cdot}422297.$$

The 2 grams of the mixture therefore contained 0·422297 gram bromide of silver, and consequently 2 − 0·422297 = 1·577703 grams chloride of silver.

It is evident from the above, that we need simply multiply the ascertained decrease of weight by

$$\frac{187{\cdot}88}{44{\cdot}49} \text{ that is, by } 4{\cdot}22297$$

to find the amount of bromide of silver originally present in the analysed mixture. And if we know this, we also know, of course, the amount of the chloride of silver; and from these data we deduce the quantities of chlorine and bromine, as directed in § 199, and the percentages as directed in § 196.

SUPPLEMENT TO I.

Remarks on Loss and Excess in Analyses, and on Taking the Average.

§ 201.

If, in the analysis of a substance, one of the constituents is estimated from the loss, or, in other words, by subtracting from the original weight of the analysed substance the ascertained united weight of the other constituents, it is evident that in the subsequent percentage calculation the sum total must invariably be 100. Every loss suffered or excess obtained in the determination of the several constituents will, of course, fall exclusively upon the one constituent which is estimated from the loss. Hence estimations of this kind cannot be considered accurate, unless the other constituents have been determined by good methods, and with the greatest care. The accuracy of the results will, of course, be the greater, the less the number of constituents determined in the direct way.

If, on the other hand, every constituent has been determined separately, it is obvious that, were the results absolutely accurate, the sum of the several constituents must be exactly equal to the original weight. Since, however, as we have seen in § 96 (Vol. I.), certain inaccuracies attach to every analysis, the sum total of the results in the percentage calculation will sometimes exceed, and sometimes fall short of, 100.

In all cases of this description, the only proper way is to give the results as actually found.

Thus, for instance, PELOUZE found, in his analysis of chromate of chloride of potassium,

Potassium	21·88
Chlorine	19·41
Chromic acid	58·21
	99·50

BERZELIUS, in his analysis of sesquioxide of uranium and potassa,

Potassa	12·8
Sesquioxide of uranium .	86·8
	99.6

PLATTNER, in his analysis of pyrrhotine,

	Of Fahlun.		Of Brasil.
Iron . .	59·72	...	59·64
Sulphur .	40·22	...	40·43
	99·94	...	100·70

It is altogether inadmissible to distribute any chance deficiency or excess proportionately among the several constituents of the analysed compound, as such deficiency or excess of course never arises from the several estimations in the same measure; moreover, such "cooking" of the analysis deprives other chemists of the possibility of judging of its accuracy. No one need be ashamed to confess having obtained somewhat too little or too much in an analysis, provided, of course, the deficiency or excess be confined within certain limits, which differ in different analyses, and which experts always know how to fix properly.

In cases where an analysis has been made twice or more, it is usual to take the mean as the correct result. It is obvious that such an average deserves the greater confidence the less it differs from the individual results, which should also be given, or, at all events, the maximum and minimum.

Since the accuracy of an analysis is independent of the quantity of substance employed (provided always this quantity be not altogether too small), the mean is to be taken quite independently of the quantities used; in other words, you must not add together the quantities used, on the one hand, and the weights obtained in the several analyses on the other, and deduce from these data the percentage amount; but the latter must be calculated from each analysis separately, and the mean of the results taken.

Suppose a substance, which we will call AB, contains 50 per cent. of A; and suppose 2 analyses of this substance have given the following results:—

(1) 2 grams AB gave 0·99 gram of A.
(2) 50 „ „ 24·00 „

From 1, it follows that AB contains 49·50 per cent of A.
„ 2, „ „ 48·00 „

Total . . . . 97·50
Mean . . . . 48·75

It would be quite erroneous to say

2 + 50 = 52 of AB gave 0·99 + 24·00 = 34·99 of A,

therefore 100 of AB contain 48·06 of A;

for it will be readily seen that this way of calculating almost completely destroys the influence of the more accurate analysis (1) upon the average, on account of the proportionally small amount of substance used.

II. Deduction of Empirical Formulæ.

§ 202.

If the percentage composition of a substance is known, a so-called empirical formula may be deduced from this; that is, the relative proportion of the several constituents may be expressed in equivalents in a formula which, upon recalculation in per-cents, will give numbers corresponding exactly, or nearly so, with those obtained by the analysis. We are compelled to confine ourselves to the expression of empirical formulæ, in the case of all substances of which we cannot determine the equivalent, such as woody fibre, mixed substances, &c.

The method of deducing empirical formulæ is very simple, and will be readily understood from the following considerations:—

How should we proceed to find the relative number of equivalents in carbonic acid?

We should say:—

The equivalent of the oxygen is to the amount of oxygen in the equivalent of carbonic acid, as 1 is to x, that is, to the number of equivalents of oxygen contained in carbonic acid;

$$8 : 16 :: 1 : x \qquad \therefore x = 2.$$

In the same manner we should find the number of equivalents of carbon by the following proportion:—

$$\begin{array}{lllll} 6 & : & 6 & :: 1 : x & \therefore x = 1. \\ \text{(eq. of carbon)} & & \text{(carbon in one eq.} & & \\ & & \text{of carbonic acid)} & & \end{array}$$

Now let us suppose we did not know the equivalent of carbonic acid but simply its percentage composition, viz.,

27·273 carbon
72·727 oxygen

100·000 carbonic acid

the relative proportion of the equivalents might still be ascertained, even though any other given number, say 100, be selected for the equivalent of carbonic acid. Let us suppose we adopt 100 as the equivalent of carbonic acid; thus,

$$\begin{array}{lllll} 8 & : & 72{\cdot}727 & :: 1 : x & \therefore x = 9{\cdot}0910 \\ \text{(eq. of oxygen)} & & \text{(amount of oxygen in} & & \\ & & \text{the assumed eq. 100)} & & \end{array}$$

and

$$\begin{array}{lllll} 6 & : & 27{\cdot}273 & :: 1 : x & \therefore x = 4{\cdot}5455 \\ \text{(eq. of carbon)} & & \text{(amount of carbon in} & & \\ & & \text{the assumed eq. 100)} & & \end{array}$$

We see here that although the *numbers* which express the relative proportion of the equivalents of oxygen and carbon have changed, yet the *relative proportion* itself remains the same; since

$$4{\cdot}5455 : 9{\cdot}0910 :: 1 : 2.$$

The process may accordingly be expressed in general terms as follows:

Assume any number, say 100 (because this is the most convenient), as the equivalent of the compound, and ascertain how often the equivalent of each constituent severally is contained in the amount of the same constituent present in 100 parts. When the numbers expressing the relative proportion of the equivalents have been found, an empirical formula has actually been deduced. Still, it is usual to reduce the numbers found to the simplest expression.

Now let us take a somewhat complicated case, for example, the calculation of the empirical formula for mannite.

The percentage composition of mannite is

39·56 of carbon
7·69 of hydrogen
52·75 of oxygen

100·00

This gives the following proportions:—

$$6 : 39{\cdot}56 :: 1 : x \qquad \therefore x = 6{\cdot}593$$
$$1 : 7{\cdot}69 :: 1 : x \qquad \therefore x = 7{\cdot}690$$
$$8 : 52{\cdot}75 :: 1 : x \qquad \therefore x = 6{\cdot}593$$

We have now the empirical formula for mannite, viz.,

$$C_{6{\cdot}593}\,H_{7{\cdot}690}\,O_{6{\cdot}593}.$$

A glance shows that the number of the equivalents of the carbon is equal to that of the equivalents of the oxygen; and the question is now whether the relative proportion found may not be expressed by smaller numbers.

A simple calculation suffices to answer this question, viz.,

$$6{\cdot}593 : 7{\cdot}690 :: 60 : x.$$

(Any other number might be substituted for 60, as the third term of the proportion, but 60 is very suitable, since it is divisible without remainder by most of the numbers.)

$$x = 70.$$

We have accordingly now the simple formula,

$$C_{60}H_{70}O_{60} = C_6H_7O_6.$$

The percentage composition of mannite given above having been previously calculated from the formula, of course there can be no doubt as to the correctness of the latter. Now let us take the results of an actual analysis.

By the combustion of 1·593 grams mannite, with oxide of copper, OPPERMANN obtained 2·296 carbonic acid and 1·106 water. This gives in per-cents,

39·31	carbon
7·71	hydrogen
52·98	oxygen
100·00	

which calculated as above, gives

$$C_{6{\cdot}552}\,H_{7{\cdot}710}\,O_{6{\cdot}622}.$$

as the first expression of the empirical formula; and by the proportion:

$$6{\cdot}552 : 7{\cdot}710 :: 6 : x \qquad \therefore x = 7{\cdot}06.$$

A glance at these numbers shows that 7·06 may be properly exchanged for 7, and also that the difference between 6·552 and 6·622 is so trifling that both may be expressed by the same number. These considerations lead therefore likewise to the formula

$$C_6H_7O_6.^*$$

The proof whether the formula is correct or not is obtained by its recalculation in per-cents. The less the calculated percentage differs from that found, the more reason there is to believe in the correctness of the formula. If the difference is greater than can be accounted for by the defects inherent in the methods, there is every reason to believe the formula to be incorrect and to establish another; for it will be readily seen that, in the case of substances of which the equivalent is not known, different formulæ may be deduced from one and the same analysis, or from several which agree closely; since the numbers found are never absolutely correct, but only approximate.

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* *Note by the Editor.*—A convenient method for calculating the empirical formulæ of organic compounds containing carbon, oxygen, and nitrogen, is given by Armstrong and Groves in Miller's Elements of Chemistry, Pt. III., Section I. p. 35.

Thus, for instance, in the case of mannite:

Calculated for		Calculated for		Found
C_6	39·56	C_8	39·67	39·31
H_7	7·69	H_9	7·44	7·71
O_6	52·75	O_8	52·89	52·98
	100·00		100·00	100·00

III. Deduction of Rational Formulæ.

§ 203.

If both the percentage composition and the equivalent of a substance are known, it is easy to reduce its *rational* formula—that is, a formula expressing not only the relative proportion of the equivalents, but also their absolute number in one equivalent of the substance.

The following examples may serve for illustration:—

1. *Deduction of the Rational Formula of Hyposulphuric Acid.*

In the first place, the percentage composition of hyposulphuric acid has been found by analysis, and, in the second place, that of hyposulphate of potassa, viz.,

Sulphur	44·44	Potassa	39·562
Oxygen	55·56	Hyposulphuric acid . .	60·438
Hyposulphuric acid	100·00	Hyposulphate of potassa	100·000

(Equivalent of potassa = 47·13)

Now:

$$39{\cdot}562 : 60{\cdot}438 :: 47{\cdot}13 : x \qquad \therefore x = 72$$

Hence 72 is the sum of the equivalents of the constituents of hyposulphuric acid—in other terms, the equivalent of hyposulphuric acid.

Having thus ascertained the correct equivalent of hyposulphuric acid, it is not necessary to assume a hypothetical one, as we had to do in the case of mannite.

Thus we may state at once:

$$100 : 44{\cdot}44 :: 72 : x \qquad \therefore x = 32$$

that is = the sum of the equivalents of the sulphur; and again:

$$100 : 55{\cdot}56 :: 72 : x \qquad \therefore x = 40;$$

that is = the sum of the equivalents of the oxygen.

Now the equivalent of sulphur, 16, is contained twice in 32; and the equivalent of oxygen, 8, is contained five times in 40; the rational formula for hyposulphuric acid is therefore,

$$S_2O_5.$$

2. *Deduction of the Rational Formula of Benzoic Acid.*

Stenhouse obtained 0·9575 carbonic acid and 0·1698 water from 0·3807 hydrated benzoic acid, dried at 100°.

0·4287 benzoate of silver, dried at 100°, gave 0·202 silver. From these numbers the following percentage compositions are calculated :—

Carbon	68·67	Oxide of silver	50·67
Hydrogen	4·95	Benzoic acid	49 33
Oxygen	26·38		
		Benzoate of silver	100·00
Hydrated benzoic acid	100·00		

(Equivalent of the oxide of silver = 115·93)

50·64 : 49·33 :: 115·93 : x $\therefore x = 112·864$

that is, the equivalent of anhydrous benzoic acid; that of the hydrated acid accordingly = 112·864 + 9 = 121·864; we say therefore now:

100 : 68·67 :: 121·864 : x $\therefore x = 83·684$
100 : 4·95 :: 121·864 : x $\therefore x = 6·032$
100 : 26·38 :: 121·864 : x $\therefore x = 32·148$

6 is contained in	83·684	13·95 times	
1 „	6·032	6·03 „	
8 „	32·148	4·02 „	

A glance at these quotients suffices to show that 13·95 may be exchanged for 14, 6·03 for 6, and 4·02 for 4. The rational formula for the hydrate of benzoic acid is accordingly,

$$C_{14}H_6O_4.$$

	This gives, by calculation,	The numbers found were,
C	68·85	68·67
H	4·92	4·95
O	26·23	26·38
	100·00	100·00

3. *Deduction of the Rational Formula of Theine.*

Stenhouse's analysis of theine, free from water of crystallization, gave the following results :—

1. 0·285 gram substance gave 0·5125 carbonic acid and 0·132 water.

2. Combustion with oxide of copper gave a mixture of CO_2 and N, in the proportion of 4 of the former to 1 of the latter.

3. 0·5828 gram of the double salt of hydrochloride of theine and bichloride of platinum, gave 0·143 platinum.

These numbers give the following as the percentage composition :—

Carbon	49·05
Hydrogen	5·14
Nitrogen	28·61
Oxygen	17·20
	100·00

and 195·83 as the equivalent of theine. For there is every reason to suppose that the composition of the double salt of hydrochloride of theine and bichloride of platinum is

$$\text{Theine} + \text{H Cl} + \text{Pt Cl}_2.$$

The equivalent of this double salt is found by the following proportion :

0·143 : 0.5828 :: 98·59 (eq. platinum) : x ∴ x = 401·80

and consequently the equivalent of theine, by subtracting from 401·80 the sum of 1 eq. bichloride of platinum (169·51) and 1 eq. hydrochloric (acid 36·46).

$$401{\cdot}80 - (169{\cdot}51 + 36{\cdot}46) = 195{\cdot}83.$$

This supplies the following proportions :—

100 : 49·05 :: 195·83 : x ∴ x = 96·054
100 : 5·14 :: 195·83 : x ∴ x = 10·066
100 : 28·61 :: 195·83 : x ∴ x = 56·027
100 : 17·20 :: 195·83 : x ∴ x = 33·683

6 is contained in 96·054, 16·01 times
1 „ 10·066, 10·07 „
14·04 „ 56·027, 3·99 „
8 „ 33·683, 4·21 „

for which numbers must be substituted, 16, 10, 4, and 4, respectively, and we get the following formula :

$$C_{16}H_{10}N_4O_4$$

This gives by calculation,		Found.
C	49·45	49·05
H	5·15	5·14
N	28·92	28·61
O	16·48	17·20
	100·00	100·00

The double hydrochloride of theine and bichloride of platinum gives platinum in 100 parts,

Calculated.	Found.
24·57	24·54

4. *Special Method of Deducing Rational Formulæ for Oxygen Salts.*

a. In the Case of Compounds containing no Isomorphous Constituents.

The rational formulæ for oxygen salts also may be deduced by a method different from the foregoing—viz., by ascertaining the ratio which the respective quantities of oxygen bear to each other. This method is exceedingly simple.

In an analysis of crystallized sulphate of soda and ammonia, the author found,

Soda	17·93
Oxide of ammonium . .	15·23
Sulphuric acid	46·00
Water	20·84
	100·00

31·04 of NaO	contain	8 of O,	consequently	17·93 of NaO	contain	4·62 of O.
26·04 ... NH_4O	...	8 ... O,	...	15·23 ... NH_4O	...	4·68 ... O.
40 ... SO_3	...	24 ... O,	...	46·00 ... SO_3	...	27·60 ... O.
9 ... HO	...	8 ... O,	...	20·84 ... HO	...	18·52 ... O.

Now

$$4{\cdot}62 : 4{\cdot}68 : 27{\cdot}60 : 18{\cdot}52 = 1 : 1{\cdot}01 : 5{\cdot}97 : 4{\cdot}01 = 1 : 1 : 6 : 4,$$

and this leads to the formula

$$NaO,NH_4O,2SO_3 + 4HO$$
$$\text{or, } NaO,SO_3 + NH_4O,SO_3 + 4\text{ aq.}$$

b. In the case of Compounds containing Isomorphous (or generally—mutually replacing) Constituents.

It is a well-known fact that isomorphous constituents may replace each other in all proportions; therefore, in establishing a formula for compounds containing isomorphous constituents, the latter are taken *collectively;* that is, they are expressed in the formula as *one and the same* body. This occurs very frequently in the calculation of formulæ for minerals.

A. Erdmann found in monradite

		Amount of Oxygen.	
Silicic acid	56·17		29·957
Magnesia	31·63	12·652	14·601
Protoxide of iron	8·56	1·949	
Water	4·04		3·590
	100·40		

Now

$$3{\cdot}59 : 14{\cdot}601 : 29{\cdot}957 = 1 : 4{\cdot}07 : 8{\cdot}3 = 1 : 4 : 8.$$

Designating 1 eq. metal by R, we obtain from these numbers the formula:—

$$4\,(RO,SiO_2) + HO \text{ or } 4\left(\left.\begin{matrix}Mg\\Fe\end{matrix}\right\}O,SiO_2\right) + aq.$$

Not only isomorphous substances, but generally all bodies of analogous composition are capable of replacing each other in compounds; thus we find that KO, NaO, CaO, MgO, &c., replace each other. These substances likewise must be expressed collectively in the formula.

Abich found in andesine.

		Amount of Oxygen.	
Silicic acid	59·60		31·79
Alumina	24·28	11·22	11·70
Sesquioxide of iron	1·58	0·48	
Lime	5·77	1·61	3·90
Magnesia	1·08	0·43	
Soda	6·53	1·68	
Potassa	1·08	0·18	
	99·92		

Now

$$3{\cdot}90 : 11{\cdot}70 : 31{\cdot}79 = 1 : 3 : 8{\cdot}15 = 1 : 3 : 8.$$

Designating 1 eq. metal by R, we obtain from these numbers the formula:—

$$RO + R_2O_3 + 4SiO_2$$
$$= RO,SiO_2 + R_2O_3,3SiO_2,$$

which may likewise be written:—

$$\left.\begin{matrix}Ca\\Mg\\Na\\K\end{matrix}\right\} O,SiO_2 + \left.\begin{matrix}Al_2\\Fe_2\end{matrix}\right\} O_3,3SiO_2.$$

Showing that this mineral is analogous in composition to leucite ($KO,SiO_2 + Al_2O_3,3SiO_2$). In andesine the potassa of the leucite is in great part replaced by lime, the soda by magnesia, and a part of the alumina by sesquioxide of iron.

What has here been said respecting the deduction of formulæ for oxygen salts, applies equally to metallic sulphides.

IV. Calculation of the Vapour-Density of Volatile Bodies, and Application of the Results, as a Means of controlling the Analysis, and of determining their Equivalents.

§ 204.

The specific gravity of a compound gas is equal to the sum of the specific gravities of its constituents in one volume.

For example, 2 volumes of hydrogen gas and 1 volume of oxygen gas give 2 volumes of aqueous vapour. If they gave simply 1 volume of aqueous vapour, the specific gravity of the latter would be equal to the sum total of the specific gravity of the oxygen and double the specific gravity of the hydrogen—viz.,

$$\begin{aligned} 2 \times 0{\cdot}0691 &= 0{\cdot}1382 \\ &+ 1{\cdot}1056 \\ \hline &= 1{\cdot}2438 \end{aligned}$$

But as they give 2 volumes of aqueous vapour, this 1·2438 is distributed between the two volumes; accordingly the specific gravity of the vapour is

$$\frac{1{\cdot}2438}{2} = 0{\cdot}6219$$

It will be readily seen that the knowledge of the vapour-density of a compound supplies an excellent means of controlling the correctness of the relative proportions of the equivalents assumed in a formula, provided that it has been correctly determined at a temperature at least 30° to 40° above the boiling-point of the substance; for it is only under these conditions that the vapour-density is constant, and to be regarded as the true one.

For instance: the results of the ultimate analysis of camphor, gives the empirical formula:

$$C_{10}H_8O.$$

Dumas found the vapour-density of camphor = 5·3136. Now, by what means can we ascertain whether this formula is correct with respect to the relative proportions of the equivalents?

Specific gravity of the vapour of carbon . .	0·8292
„ „ hydrogen gas	0·0691
„ „ oxygen gas	1·1056

$$\begin{array}{rl}
10 \text{ eq. } C = 10 \text{ volumes} = 10 \times 0{\cdot}8292 = & 8{\cdot}2922 \\
8 \text{ eq. } H = 16 \text{ volumes} = 16 \times 0{\cdot}0691 = & 1{\cdot}1056 \\
1 \text{ eq. } O = 1 \text{ volume} = 1 \times 1{\cdot}1056 = & 1{\cdot}1056 \\
\hline
& 10{\cdot}5034
\end{array}$$

This sum is almost exactly twice as large as the vapour-density found by direct experiment ($\frac{10{\cdot}5034}{2} = 5{\cdot}252$); which shows that the relative proportions of the equivalents are correctly given in the empirical formula of camphor. But whether the formula is correct, also, with regard to the absolute number of equivalents, cannot be determined simply from the vapour-density, because we do not know to how many volumes of camphor vapour 1 equivalent of camphor corresponds. Liebig assumed the equivalent of camphor to correspond with 2 volumes, and gives accordingly the formula $C_{10}H_8O$; whilst Dumas assumes it to correspond with 4 volumes, and accordingly gives the formula $C_{20}H_{16}O_2$.

The knowledge of the vapour-density affords, therefore, in reality, simply a means of controlling the correctness of the analysis, but not of establishing a rational formula; and although it is sometimes made to serve the latter purpose, yet this can be done only in the case of substances for which we are able to infer from analogy a certain ratio of condensation: thus, for instance, experience proves that 1 equivalent of the hydrates of the volatile organic acids, of alcohols, &c., corresponds to 4 volumes.

In § 203, 2, we have found the rational formula of hydrated benzoic acid to be $C_{14}H_6O_4$. Dumas and Mitscherlich found the vapour-density to be 4·26.

Now nearly the same number is obtained by dividing by 4 the sum total of the vapour-densities of the several constituents contained in 1 equivalent of hydrated benzoic acid, viz.,

$$\begin{array}{rl}
14 \text{ volumes } C = & 11{\cdot}609 \\
12 \text{ volumes } H = & 0{\cdot}829 \\
4 \text{ volumes } O = & 4{\cdot}422 \\
\hline
\end{array}$$

$$\frac{16{\cdot}860}{4} = 4{\cdot}215$$

Hermann Kopp* has called attention to the fact that, if the equivalent of a substance referred to H = 1, and the vapour-density of the same to atmospheric air = 1, the division of the equivalent by the vapour-density gives the following quotients,

28·944 14·472 7·236

according as the formula corresponds with 4, 2, or 1 volume of vapour:

28·944 corresponds with a condensation to 4 volumes
14·472 „ „ „ 2 „
7·236 „ „ „ 1 volume

Kopp calls these numbers *normal quotients.* If the vapour-density is not quite exact, but merely approximate (determined by experiment), other numbers are found instead of these, but they should be very close.

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* Compt. rend. 44, 1347; Chem. Centralbl. 1857, 594.

If, therefore, the equivalent of a body is known, we may, with the greatest facility, ascertain whether the determination of the vapour-density of the body has given approximately correct results or not.

Gay-Lussac found the vapour-density of alcohol to be 1·6133; Dalton, 2·1.* Now, which is the correct number?

The equivalent of alcohol, $C_4H_6O_2$, is 46.

$$\frac{46}{2{\cdot}1} = 21{\cdot}9$$

$$\frac{46}{1{\cdot}6133} = 28{\cdot}5$$

It is evident that Gay-Lussac's number is approximately correct, for the quotient found by it comes very near the normal quotient, 28·944.

Again, if the equivalent of a body is known, and also the number of volumes of vapour corresponding with 1 equivalent, it is very easy to calculate the theoretical vapour-density of the body. For instance: the equivalent of hydrated benzoic acid is 122: this number divided by 28·944 gives 4·215 as the vapour-density, which is the same as that found by actual experiment.

Lastly, if the vapour-density of a body is known approximately (that is, by experiment), and also the ratio of condensation, the equivalent of the body may be calculated approximately by the aid of these quotients.

For example: Boullay and Dumas found the vapour-density of acetic ether to be 3·06: this number multiplied by 28·944 gives 88·56 as the equivalent of acetic ether, which comes near the actual equivalent, 88.

Having thus shown how the knowledge of the vapour-density of a body may be used for controlling the results of the ultimate analysis, we will proceed to show how the vapour-density is calculated from the data obtained as described in § 194, *A* and *B*.

A. We will take as an illustration Dumas' estimation of the density of camphor vapour.

The results of the experiment were as follows:—

Temperature of the air	13·5°
Barometer	742 mm.
Temperature of the bath at the moment of sealing the globe	244°
Increase of the weight of the globe	0·708 grm.
Volume of mercury entering the globe	295 c.c.
Residual air	0

Now, to find the vapour-density, we have to determine three things:—

1. The weight of the air which the globe holds (as a necessary step to the determination of 2).

2. The weight of the camphor vapour which the globe holds.

3. The volume with which the camphor vapour corresponds, at 0° and 760 mm.

The solution of these questions is quite simple; and if the calculation, notwithstanding, appears somewhat complicated, this is merely owing to certain reductions and corrections which are necessary.

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* Gmelin's Handbook, 8, 199.

1. *The weight of the air in the globe.*

The globe holds 295 c. c., as we see by the volume of mercury required to fill it.

First, what will the volume of 295 c. c. of air measured at 13·5° and 742 mm., be at 0° and 760 mm.?

The question is solved according to the directions in § 198, as follows:—

$760 : 742 :: 295 : x \qquad \therefore x = 288$ c. c. (at 13·5° and 760 mm.)

and again:

$$\frac{288}{1 + (13{\cdot}5 \times 0{\cdot}00366)} = \frac{288}{1{\cdot}04941} = 274 \text{ c. c. (at } 0^\circ \text{ and } 760 \text{ mm.)}$$

Now 1 c. c. of air at 0° and 760 mm. weighs 0·0012936 gram; 274 c. c. will weigh 0·0012936 × 274 = 0·35444 gram.

2. *The Weight of the Vapour.*

At the beginning of the experiment, we tared the globe + the air within it; we afterwards weighed the globe + the vapour (but without the air);—to find, therefore, the actual weight of the vapour, it is not sufficient to subtract the tare from the weight of the globe filled with vapour, since (*glass* + *vapour*)—(*glass* + *air*) is not = *vapour;* but we have either to subtract, in the first place, the weight of the air from the tare, or to add the weight of the air to the increase of the weight of the globe. Let us do the latter:—

Weight of air in the globe . .	=	0·35444 gram
Increase of weight of globe . .	=	0·70800 gram
The weight of the vapour is accordingly	=	1·06244 gram

3. *The Volume to which this Weight of* 1·06244 *gram of Vapour corresponds at* 0° *and* 760 *mm.*

From the data given above, we know that this weight corresponds with 295 c. c. at 244°, and 742 mm. Before we can proceed to reduce this volume according to the directions in § 198, the following corrections are necessary:—

a. 244° of the mercurial thermometer correspond, according to the experiments of MAGNUS, with 239° of the air thermometer (see Table VI.).

b. According to DULONG and PETIT, glass expands (commencing at 0°) $\frac{1}{35000}$ of its volume for each degree C. The volume of the globe at the moment of sealing was accordingly—

$$295 + \frac{295 \times 239}{35000} = 297 \text{ c. c.}$$

If we now proceed to reduce this volume to 0° and 760 mm. we find by the proportion,

$$760 : 742 :: 297 : x$$

x (that is, c. c. of vapour at 760 mm. and 239°) = 290;
and by the equation,

$$\frac{290}{1 + (239 \times 0{\cdot}00366} = x$$

x (that is, c. c. of vapour at 760 mm. and 0°) = 154·6.

154·6 c. c. camphor vapour at 0° and 760 mm., therefore, weigh 1·06244 gram, and consequently 1 litre (1000 c. c.) weighs 6·87218 grams; since

$$154{\cdot}6 : 1{\cdot}06244 :: 1000 : 6{\cdot}87218.$$

Now 1 litre of air at 0° and 760 mm. weighs 1·2936 gram, and consequently the density of the camphor vapour is 5·31245; since

$$1{\cdot}29361 : 6{\cdot}87218 :: 1 : 5{\cdot}31245.$$

B. Estimation of the vapour-density of ether by the HOFMANN-WICHELHAUS method.

Ether used	·0724 gram.
Heated to	100°
Volume read off	49·201 c. c.
Barometer	754 mm.
Temperature of air	20°
Height of mercurial column after heating to 100°	300 mm.
Tension of mercury at 100°	746 mm.

The volume read off at 100° requires correction for the expansion of the glass. Glass expands for each degree $\frac{1}{35000}$ of its volume, therefore the corrected volume of the vapour will be

$$49{\cdot}201 + \frac{49{\cdot}201 \times 100}{35000} = 49{\cdot}342.$$

This volume must now be reduced from 100° to 0°. According to § 198, 49·342 c. c. at 100° become

$$\frac{49{\cdot}342}{1 + (0{\cdot}003665 \times 100)} = 36{\cdot}108 \text{ c. c. at } 0^\circ.$$

and the pressure at which the volume was read off; this pressure equals the height of the barometer *minus* the height of the mercurial column at 100° and the tension of mercury at 100°.

But as we read the barometer at 20°, this must first be reduced to 0°. The co-efficient of expansion of mercury is 0·00018, therefore the 754 mm. of pressure at 20° become

$$\frac{754}{1 + (0{\cdot}00018 \times 20)} = 751{\cdot}295 \text{ mm. at } 0^\circ.$$

The mercurial column of 300 mm. at 100° becomes

$$\frac{300}{1 + (0{\cdot}00018 \times 100)} = 294{\cdot}695 \text{ mm.}$$

at 0°. The tension of mercury at 100° = 0·746 mm. Consequently the actual pressure

$$= 751{\cdot}295 - (294{\cdot}695 + 0{\cdot}746) = 455{\cdot}854 \text{ mm.}$$

The 36·108 c. c. at 455·854 mm. pressure have now to be reduced to 760 mm. pressure, thus—

$$760 : 455{\cdot}854 :: 36{\cdot}108 : x \qquad \therefore x = 21{\cdot}6579$$

1000 c. c. air at 0° and 760 mm. weigh 1·2936 gram, therefore 21·6579 c. c. air weigh ·0280 gram. Now the weight of 21·6579 c. c. ether has been found to be ·0724 gram. Therefore the vapour-density required is

$$\frac{{\cdot}0724}{{\cdot}0280} = 2{\cdot}586$$

PART II.

SPECIAL PART.

I. ANALYSIS OF WATERS.

A. ANALYSIS OF POTABLE WATERS (SPRING-WATER, RIVER-WATER, &c.).*

§ 205.

THE analysis of the several kinds of fresh water is *usually* restricted to the quantitative estimation of the following substances :—

a. Dissolved substances.
  α. *Inorganic.*
    Bases : Soda, ammonia, lime, magnesia.
    Acids and Halogens : Sulphuric, nitric, nitrous, silicic, carbonic acids, and chlorine.
  β. *Organic.*
    Acids of humus and other organic matters.

b. Suspended substances.
    Clay, &c.

The estimation, therefore, of these bodies alone will be considered here. If the examination is to be extended to other constituents, the methods given in §§ 206—213 must be resorted to.

I. The Water is Clear.

1. Determination of Chlorine.

This may be effected, either, *a*, in the gravimetric, or, *b*, in the volumetric way.

a. Gravimetrically.—500—1000 grams or c. c.† are taken, acidified with nitric acid, and precipitated with nitrate of silver. The precipitate should be protected from light and not filtered off until it has completely subsided (§ 141, I., *a*, Vol. I.). If the quantity of the chlorine is so small that the silver solution produces only a slight turbidity, a larger portion of the water is evaporated to $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{6}$, &c., of its bulk, filtered, the precipitate washed, and the filtrate treated as directed.

b. Volumetrically.—1000 grams or c. c. are evaporated to a small bulk, and the chlorine determined in the residual liquid, without previous filtration, by solution of nitrate of silver, with addition of chromate of potassa (§ 141, I., *b*, *a*, Vol. I.).

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* Compare Qualitative Analysis, p. 289, *et seq.*

† As the specific gravity of fresh water differs but little from that of pure water, the several quantities of water may safely be measured instead of weighed in ordinary determinations. The calculation is facilitated by taking a round number of c. c.

2. Determination of Sulphuric Acid.

1000 grams or c. c. of the water is acidified with hydrochloric acid distinctly, but not too strongly, and chloride of barium is added in slight excess; when the precipitate has completely subsided (§ 132, I., 1, Vol. I.) it is collected. If the quantity of sulphuric acid is very small, the acidified water is evaporated to $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{6}$, &c., of the bulk, before adding the chloride of barium. The filtrate may be used for estimating the soda, § 205 (7).

3. Determination of Nitric Acid.

A. Of the methods described in § 149 (Vol. I.), only those which give good results in presence of organic matter are suited for the *exact estimation* of nitric acid in water. SCHLÖSING's method, p. 395 (Vol. I.), F. SCHULZE's as described by WULFERT (p. 397, Vol. I.), and also F. SCHULZE's given on p. 399 (Vol. I.), are more particularly serviceable.

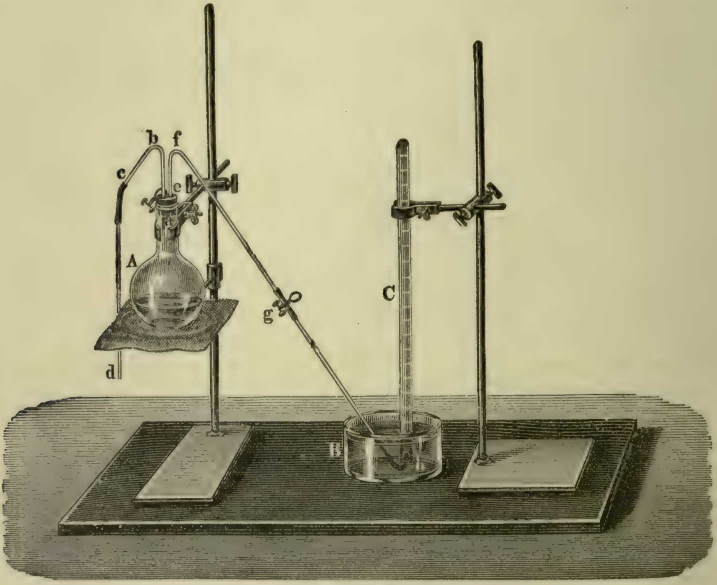

Fig. 76

The second method (p. 397), in which the nitric oxide is collected and measured over mercury, requires a rather deep trough, holding a considerable quantity of mercury, and a special cylinder at the top provided with a glass stop-cock. The accuracy of the results is thoroughly satisfactory. TIEMANN,* without diminishing the precision of the method, has greatly simplified it by substituting well-boiled soda solution for the mercury. This modified process is suitable for the accurate estimation of nitric acid in water.

A (fig. 76) is a flask of about 150 c. c. The tube *c b a* is drawn out not too finely to a point at *a*, which projects about 2 cm. below the caoutchouc stopper. The orifice of the tube *e f g* on the other hand is flush with the lower surface of the stopper. The end of the tube *g h* is protected by a piece of flexible tubing drawn over it. The trough *B* and the tube *C* are filled with boiled solution of soda of 10 per cent. *C* is divided into tenths of c. c., and should be as narrow as convenient.

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* Anleitung zur Untersuchung, von Wasser von W. KUBEL, zweite auflage, von T. TIEMANN. Braunschweig: Vieweg u. Sohn, 1874, p. 55.

100 to 300 c. c. of the water—occasionally more—are evaporated in a dish to about 50 c. c., and transferred to *A*, the dish being repeatedly rinsed with small quantites of water. If any precipitate has been formed during the evaporation it is not necessary that it should all be transferred to *A*.

The tubes are left open and the water is boiled down further, the orifice of *e f g h* being placed under the soda in the trough towards the end of the operation. After a few minutes the flexible tube at *g* is pressed between the fingers. If the whole of the air has been expelled by the steam, the soda solution will rise suddenly in the tube and a slight concussion will be felt by the fingers: if this is the case the clip is put on at *g* and the steam allowed to escape at *d*. The boiling continued until the contents of the flask are reduced to about 10 c. c. The lamp is now removed, *c* is closed with a clip, and the tube *d c* is filled with water with a wash-bottle, if an air bubble remains at *c*, it must be removed by pressing with the fingers.

The measuring tube *C* is now placed over the orifice of *e f g h*, so that the latter may rise 2 or 3 cm. into the former. As soon as the flexible tubes at *c* and *g* collapse owing to the external pressure, some nearly saturated solution of protochloride of iron containing free hydrochloric acid is poured into a small beaker, which has two marks on its upper part, the space between them indicating a capacity of 20 c. c.; some concentrated hydrochloric acid is put likewise into another beaker. The tube *d* is now dipped into the iron solution, and by opening the clip at *c*, 15 or 20 c. c. are allowed to enter the flask, *d* is then dipped into the hydrochloric acid, which is allowed to ascend the tube twice in small quantities so as to rinse the iron solution out of *d c b a*. A small bubble of hydrochloric acid gas frequently forms at *b*, which, however, will disappear as soon as the pressure in the flask increases.

The flask *a* is now warmed over a lamp, at first very gently, until the flexible tubes at *c* and *g* are slightly puffed out, the pressure of the fingers is then substituted for that of the clip at *g*, and as soon as the pressure increases, the nitric oxide evolved is allowed to pass over into the measuring tube. Finally the heat is raised until the volume of gas in *C* ceases to increase and the delivery tube is then removed from the trough. The operation should not be hurried towards the end, so that the hydrochloric acid may be perfectly absorbed. Of course the india-rubber joints must be absolutely air-tight: this can only be secured by binding them with wire. (F. HESS.)*

Having closed the measuring tube *C* with your thumb and shaken it well, it is transferred to a large glass jar containing water at 15–18°, immersed therein, and the volume finally read off in the usual way (§ 15, Vol. I.), noting the temperature of the water and the barometrical pressure. The volume of gas in c. c. reduced to 0° and 760 mm., allowing for the tension of aqueous vapour (§ 198), when multiplied by 2·413 gives the amount of nitric acid present in milligrammes.

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* Zeitschr. f. anal. Chem. 13, 260.

If nitrous acid is present in sufficient quantity to be estimated it will be included in the result and a correction must be made by subtracting from it 1·421 parts for every 1 part of nitrous acid present.

B. For the *approximate estimation* of nitric acid in water, MARX's* process is used with certain modifications. This, like the older process of BOUSSINGAULT,† is based on the decolorisation of indigo by nitric acid; BOUSSINGAULT makes the determination in a hydrochloric acid solution and heats, whilst MARX uses a large quantity of concentrated sulphuric acid, which develops heat as it mixes with the water: the process has the advantage of being very rapid. It has been further studied by H. TROMMSDORFF,‡ F. GOPPELSRÖDER,§ H. STRUVE,‖ VAN BEMMELEN,¶ R. WARINGTON,** KUBEL and TIEMANN,†† SUTTON‡‡ and others.

Before describing the modification of the process which has given the best results in the author's laboratory, some important observations drawn from the memoirs just cited may be briefly alluded to, which show that the results of titration with indigo solution can only be used under very definite conditions, and cannot by any means lay claim to perfect accuracy.

a. The quanty of indigo oxidized by a given quantity of nitric acid, is the same only when the conditions under which the reaction takes place (dilution, temperature, amount of sulphuric acid, &c.,) are identical.

b. Other conditions being identical, much less indigo is oxidized if it is added gradually after the water has been mixed with sulphuric acid, than if it is added in proper amount before mixing with sulphuric acid (VAN BEMMELEN).

c. The same conditions should be observed in titrating the indigo solution and in using it for the estimation of nitric acid, namely, those under which the largest amount of indigo is oxidized.

d. As the products of the reaction are not colourless but yellowish, the liquid is coloured faintly brown as soon as the indigo begins to be in excess (if chlorides are absent), which changes to a greenish tinge with a somewhat larger excess, but of course the shades vary with the quantity of nitric acid, that is to say, with the amount of the yellow oxidation product formed, the test produced when the indigo first begins to be in excess is also influenced by the amount of sulphuric acid and by the presence of chlorides. It requires some practice, therefore, to hit the point when the reaction is complete.

e. Moreover, readily oxidizable organic matter if present in any quantity must be oxidized before the nitric acid estimation, otherwise the results will be valueless. The amount of such matter in spring water, however, is usually so small that it may be neglected.

f. If the water contains nitrous acid, this also will decolorize the indigo, and a correction will be necessary, unless its amount is very small.

There are no exact experiments showing the relative values of nitrous and nitric acids in their action on indigo. KUBEL and TIEMANN (*loc. cit.* p. 81) deduct ·473 parts nitric acid for 1 part nitrous acid.

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* Zeitschr. f. anal. Chem. 7, 412.

† Agronomie, Chimie agricole et Physiologie, 2, 244 (1862).

‡ Zeitschr. f. anal. Chem. 8, 364; 9, 171.

§ *Ib.* 9, 3; 10, 266.

‖ *Ib.* 11, 25.

¶ *Ib.* 11, 136.

** Chem. News, 35, 45 and 57.

†† *Loc. cit.*, p. 65.

‡‡ Volumetric Analysis.

g. Chlorides, in such small quantities as usually occur in spring water, have no appreciable influence on the end reaction.

Execution of the Method.

Requisites.

a. A solution of pure nitrate of potassa containing 1·8724 gram in the litre, 1 c. c. = 1 mgrm. anhydrous nitric acid (NO_5).

b. A solution of the best indigo carmine in water. It should be roughly titrated with the nitrate of potassa solution *a* in the manner described hereafter, and then diluted so that 6 to 8 c. c. = 1 mgrm. nitric acid.

c. Chemically pure sulphuric acid of sp. gr. 1·842, perfectly free from sulphurous and arsenious acids and oxides of nitrogen.

d. Several thin flasks of about 200 c. c. capacity.

e. A small cylindrical measure holding 50 c. c. and divided into c. c.

f. A Mohr's burette divided into tenths of a c. c.

g. A 25 c. c. pipette or another burette.

h. A 5 c. c. pipette divided into c. c. or half c. c.

i. A measuring flask of 250 c. c. capacity.

aa. Preliminary Trial.

25 c. c. of the water is measured off, and transferred to a flask; the 50 c. c. measure is filled with sulphuric acid and the burette with indigo solution. The sulphuric acid is added to the water all at once, shaken for a moment, and the indigo run in as quickly as possible with shaking until a permanent greenish tint is produced. If the water does not require more than 20 c. c. of indigo solution of the above strength, the water can be titrated directly, otherwise it must be diluted with a proper quantity of pure water, and subjected again to the preliminary trial.

bb. The Actual Titration.

α. 25 c. c. of the water—properly diluted if necessary—are measured and poured into a flask, and as much indigo as was used in the preliminary trial, *aa*, is added; a quantity of sulphuric acid, equal in volume to the liquid in the flask, is now measured out and added all at once, the mixture shaken, and indigo solution run in quickly out of the burette until the liquid remains permanently of a greenish tint.

β. The last experiment is repeated, adding to the water at first half a c. c. less indigo than the total quantity used, afterwards proceeding as in *α*. The final result is to be taken as correct.

γ. From the rough titration of the indigo, calculate the amount of nitrate of potassa solution corresponding with the indigo solution used in *β*, multiply the result by 10, transfer this quantity of the standard nitrate solution to a 250 c. c. flask, fill with pure water to the mark, and titrate 25 c. c. of this fluid with indigo (as in *β*). If the quantity of indigo solution used is nearly the same as that required in *β*, its exact value may be calculated, but if it does not another nitrate solution must be made up in the 250 c. c. flask, more closely resembling the water, and the titration with the indigo solution must be repeated.

δ. If the water contains any considerable amount of organic matter, it must first be destroyed by permanganate of potassa (p. 126). In this case, the estimation of the organic matter and nitric acid may be conveniently combined.

4. Determination of Nitrous Acid.

Nitrous acid frequently occurs in natural waters in minute quantities, and its estimation is of great value in forming an opinion as to the quality of a water. Good drinking water contains none.

There are two methods in use for estimating nitrous acid in waters: one colorimetric, depending on the formation of iodide of starch, and described by H. TROMMSDORFF,* the other based on the oxidation of the nitrous to nitric acid by permanganate of potassa, first described by JEAN DE SAINT GILLES,† afterwards critically tested by S. FELDHAUS,‡ and subsequently improved and specially adapted to water analysis by W. KUBEL § The two methods complement each other, the first is preferable when traces of nitrous acid only are present, the second when the water contains rather more nitrous acid (above 1 mgrm. in 100 c. c. KUBEL and TIEMANN, *loc. cit.* p. 79)

a. Iodide of Starch Method.—If pure water is mixed with pure dilute sulphuric acid, and solution of iodide of zinc and starch,|| and allowed to remain at rest *in the dark*, no blue colour is produced,¶ but if the water contains nitrous acid, the blue colour will be developed after a shorter or longer time according to the quantity of the acid present. This method requires water perfectly free from nitrous acid,** pure dilute sulphuric acid, solution of iodide of zinc and starch, solution of nitrite of potassa, 1 c. c. of which contains ·01 mgrm. NO_3,†† and four test cylinders of equal width, marked at 50 c. c.: this mark should be 15 or 16 cm. from the bottom.

a. Preliminary trial.—1 c. c. dilute sulphuric acid and 1 c. c. iodide of zinc and starch solution are added to 50 c. c of the water in one of the cylinders; this is placed on a white surface and the colour is observed by looking down through the column of liquid. If a blueness is evident before the lapse of two minutes, the water will require dilution. In this case 25, 10 or 5 c. c. are measured into a cylinder, water added to the 50 mark and the trial repeated, until at least two minutes elapse before the blue tint makes its appearance.

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* Zeitschr. f. anal. Chem. 8, 358.

† Compt. rend. 1858, 46, 624; Journ. f. prakt. Chem. 73, 473.

‡ Zeitschr. f. anal. Chem. 1, 426.

§ Journ. f. prakt. Chem. 102, 229.

|| To prepare this solution: 5 grams of starch, 20 grams of chloride of zinc, and 100 c. c. distilled water, are boiled for several hours, the water being replaced as it evaporates, until the starch envelopes are nearly all dissolved; 2 grams of dry iodide of zinc are then added, and the solution diluted to a litre and filtered. The filtration is slow, but a clear liquid is obtained, which, after some months, deposits a few flocks, but remains colourless if kept in well-closed bottles in the dark. (RICHTER, Zeitschr. f. anal. Chem. 8, 358.)

¶ In direct sunlight the acidified solution acquires a blue colour after ten minutes, but in diffused daylight only after several hours or days.

** If necessary, this may be prepared by distilling spring water with a few drops of dilute sulphuric acid, the distillate being collected in four equal parts; each of these is tested with sulphuric acid and iodide of zinc and starch, and those which are found to be quite free from nitrous acid are reserved for use.

†† Prepared by dissolving about 2·5 grams of fused nitrite of potassa to 100 c. c., 10 c. c. of this solution are diluted to 1 litre, and tested with permanganate of potassa solution (·3163 grams per litre) as directed, p. 121; it is then further diluted, so that 1 c. c. = ·0001 gram nitrous acid. 10 c. c. of this solution diluted to 100 c. c. will be the solution required of which 1 c. c. = ·00001 nitrous acid. As nitrite of potassa does not keep unaltered in solution, it must be tested occasionally.

β. Actual Analysis.—A cylinder is filled to the 50 c. c. mark with water, either as it is or diluted according to the result of *a*; into the other three cylinders are placed 0·1, 0·2 and 0·3 c. c. of the standard nitrite respectively, which are then filled up to the mark with pure water: 1 c. c. dilute sulphuric acid and 1 c. c. iodide of zinc and starch solution are added to each cylinder, and the contents mixed. If the reaction in the first cylinder occurs simultaneously with that in one of the others, and proceeds at the same rate, the two fluids contain the same quantities of nitrous acid; if not, the experiment must be repeated with solutions containing other quantities of nitrite until comparable results are obtained. At first the tints are compared as above indicated, by looking down through the column of liquid on to the white paper on which the cylinders rest, but afterwards, when the intensity of the colour increases, the two cylinders are held side by side in an inclined position, and the tint is observed by looking through sections of the same thickness on to the white paper beneath. If the amount of nitrous acid present is so small that no coloration takes place until after the lapse of 10 to 20 minutes, it is merely necessary to note the simultaneous appearance of the blue tint in the two cylinders, without observing its rate of increase. In calculating the results, it is only necessary to remember that the quantities of nitrous acid are the same in the two cylinders in which the course of the reaction is found to be similar.

b. Permanganate Method.—This method, depending on the oxidation of nitrous to nitric acid by permanganate of potassa, cannot be applied in the usual way to solutions so dilute as natural waters, and—as they often do—containing organic substances (comp. § 131, 5, Vol. I.), that is, the permanganate solution cannot be added directly to the acidified water until the pale red tint becomes permanent, as the time required for the appearance of the end reaction is so long that the permanganate would act on the organic substances present, and vitiate the result. In the following modification of the process proposed by KUBEL, the oxidation is much more rapid, so that the small quantities of organic matter present in spring water have no appreciable influence on the accuracy of the results (KUBEL and TIEMANN, *loc. cit.* p. 79).

The materials required are a solution of pure sulphate of iron and ammonia containing 3·92 grams of the pure dry crystals in a litre; the salt should be dissolved in a litre flask by the aid of a little dilute sulphuric acid in water which has been well boiled and then cooled. Also a corresponding solution of pure permanganate of potassa, that is, a solution 10 c. c. of which just oxidize 10 c. c. of the iron solution, leaving it slightly red.

In the analysis, 100 c. c. of the water are mixed with an excess of permanganate (5, 10 or 20 c. c.), 6—8 c. c. of dilute pure sulphuric acid (1 to 5) is added, and the iron solution is run in immediately until colourless, then permanganate again until the liquid is of a pale red tint, which need not be permanent.

In making the calculation, the number of c. c. iron is deducted from the total c. c. permanganate; the remainder is the permanganate used in oxidizing the nitrous acid present, each c. c. of which = 0·19 mgrm. nitrous acid.

By operating in this way, any organic matter which may be present does not appreciably affect the result.

5. Determination of Silicic Acid, Lime and Magnesia.

1000 grams or c. c. of the water acidified with hydrochloric acid are evaporated to dryness, preferably in a platinum dish, the residue treated with hydrochloric acid and water, the separated silicic acid filtered off and treated as directed in § 140, II., *a* (Vol. I.). The lime and magnesia are estimated in the filtrate as directed in § 154, 6, *a* (Vol. I.).

6. Determination of the Total Residue and Soda.

a. 1000 grams or c. c. of the water are evaporated to dryness, with proper care, in a weighed platinum dish, first over a lamp, finally on the water-bath: the residue is heated in the air-bath at about 180° until it ceases to lose weight. This gives the *total amount of the salts* (together with organic matter).

b. The residue is treated with water, and pure dilute sulphuric acid added cautiously, in moderate excess, the vessel being covered during this operation with a dish, to avoid loss from spirting; it is then placed on the water-bath, without removing the cover. After 10 minutes the cover is rinsed by means of a wash-bottle, the whole evaporated to dryness, the free sulphuric acid expelled, the residue ignited in the last stage with addition of some carbonate of ammonia (§ 97, 1, Vol. I.), and weighed. The residue consists of sulphate of soda, sulphate of lime, sulphate of magnesia, and some separated silicic acid; it should not redden moist litmus paper. The quantity of sulphate of soda is found by subtracting from the weight of the residue the known weight of the silicic acid and the weight of the sulphate of lime and sulphate of magnesia calculated from the quantities of these earths found in 5.

7. Direct Estimation of Soda.

If it is desirable to estimate the soda directly, the filtrate from the sulphuric acid determination (§ 205, 2) may be used, proceeding according to § 209.

8. The numbers found in 1—7 are calculated to 1000 parts of water, and from the data obtained the amount of carbonic acid in combination is determined in the following manner:—The quantities of sulphuric acid corresponding with the bases found are added together, and from this sum are subtracted, first, the amount of sulphuric acid precipitated from the water by chloride of barium (2), secondly, the amount corresponding with the nitric acid (and nitrous acid) found, and thirdly, the amount corresponding with the chlorine found (for 1 eq. Cl, 1 eq. SO_3); the remainder is equivalent to the carbonic acid combined with the bases in the form of *neutral* carbonates: 40 parts of sulphuric acid corresponding with 22 parts of carbonic acid.

If, by way of control, it is thought advisable to determine the combined carbonic acid directly, 1000 grams or c. c. of the water is evaporated in a flask to a small bulk; tincture of litmus is added, then standard hydrochloric or nitric acid, and the carbonic acid determined as directed Vol. I. p. 333, *bb*.

9. Control.

If the quantities of the soda, lime, magnesia, sulphuric acid, nitric acid, silicic acid, carbonic acid, and chlorine are added together, and an amount of oxygen corresponding with the chlorine (since this latter is combined with metal and not with oxide) is subtracted from the sum, the remainder should correspond closely with the total amount of the salts found in 6, *a*. *Absolute* agreement cannot be expected, since, 1, during the evaporation of the water chloride of magnesium is partially decomposed and converted into a basic salt; 2, the silicic acid expels some carbonic acid; and 3, it being difficult to free carbonate of magnesia from water without incurring loss of carbonic acid, the residue remaining upon the evaporation of the water contains the carbonate of magnesia as a basic salt, whereas, in the calculation, it has been assumed that the quantity of carbonic acid was that of the neutral salt. Moreover, the organic matter (whose actual amount can scarcely be estimated), the traces of nitrites and the influence of ammonium salts on the weight of the total residue are not taken into account.

10. Determination of free Carbonic Acid.

In the case of well-water, this may be conveniently estimated by the process described in § 139, γ (p. 334, Vol. I.): in this way that portion of the carbonic acid is determined which is contained in the water over and above the quantity corresponding with the monocarbonates, or, in other words, the carbonic acid which is free and which is combined with the carbonates to form bicarbonates.

11. Determination of Organic Matter.

Many well-waters contain so much organic matter as to be quite yellow, others contain traces, and many again may be said to be free from such substances. The exact estimation of organic matter is by no means an easy task, and the method which was once commonly employed —namely, ignition of the water residue dried at 180°, treatment with carbonate of ammonia, gentle ignition again, and calculation of the organic matter from the loss of weight—yields an entirely fallacious result, since there can be no certainty as to the condition of the magnesia in the residue either before or after ignition; the silicic acid expels carbonic acid, which is not again taken up on treatment with carbonate of ammonia, &c. As it is of great importance to know the amount of organic matter present in a water in order to judge of its quality, many chemists have endeavoured to solve this problem, but the results at present are not entirely satisfactory. FRANKLAND and ARMSTRONG* boil a measured quantity (1 litre) of the water with 30 c. c. of a saturated solution of sulphurous acid, 0·2 gram sulphite of soda and a few drops of a solution of proto- or sesquichloride of iron for two or three minutes. (In the presence of much organic matter, the flask or retort is connected with a reflux condenser.) The liquid is now evaporated to dryness in a glass dish, keeping off all dust—and the residue, which will be free from carbonic, nitric and nitrous acids is mixed with perfectly pure chromate of lead, and transferred to a combustion tube, which is then charged with oxide of copper and copper turnings, the tube being subsequently exhausted with a SPRENGEL pump, and the combustion made in the usual way, at first very slowly. The products are collected by the aid of the pump in a glass tube over a mercurial trough, and the carbonic acid, nitric oxide and nitrogen determined in the mixture by the ordinary process of gas analysis; the carbon and nitrogen of the organic matter is then calculated from the results.

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* Journ. Chem. Soc. 21, 77.

W. Dittmar and H. Robinson[*] have modified the above method, estimating the carbon and nitrogen in two separate portions of water, to one sulphurous acid is added, and to the other sulphurous acid and a little proto- or sesquichloride of iron. Both are evaporated at first in a flask placed in an inclined position and finally to dryness in a dish: sometimes a little sulphate of potassa is added to increase the bulk of the residue; the carbon and nitrogen are estimated in the respective residues by combustion. *For the carbon*, a combustion tube, is used containing a spiral of silver foil and then granulated oxide of copper, water and sulphurous acid being absorbed by two tubes, the one containing concentrated sulphuric acid with a little chromic acid, the other chloride of calcium. The silver and oxide of copper are first heated in a current of air until the latter no longer causes any turbidity with baryta water; the platinum boat containing the evaporated residue is then inserted, and the combustion carried out in a current of oxygen; a soda-lime tube (p. 35) being used to absorb the carbonic acid. Varrentrapp and Will's method (§ 186) is used for the nitrogen determination, the ammonia being estimated by the Nessler test (p. 129). F. Schulze[†], F. Bellamy,[‡] and others have previously recommended the estimation of the carbon in the evaporated residue in a similar manner. Various objections have been raised against these methods,[§] more especially that during the evaporation organic matter may be volatilized and decomposed. Nevertheless, the data afforded by these estimations may be of considerable service in forming an opinion on a water, especially if it is rather rich in organic matter.

As these methods are evidently somewhat troublesome and moreover do not completely attain their object, it is usually considered sufficient if the quantity of permanganate of potassa reduced by the organic matter in the water is estimated, or, in other words, the quantity of oxygen required to oxidize this organic matter.

Comparative experiments of this kind are of value, although they do not give a numerical expression for the quantity of organic matter present, seeing that different substances reduce different proportions of permanganate, still less do they permit any conclusion as to the fitness or unfitness of a water for drinking purposes; there can be no doubt for instance that the influence of putrefying nitrogenous matter on health will be quite different from that of humous substances.

In order to distinguish between organic matter, which is more readily and more difficultly acted on by oxidizing agents, Fleck [||] uses alkaline silver solution instead of permanganate of potassa. This method, like the permanganate method, does not give the quantity of the organic matter present,[¶] but it affords comparative numbers which may serve to characterize the water. The same, but no more, may be said of Wanklyn, Chapman, and Smith's method,[**] in which, after the ammonia existing as such has been removed, the water is boiled with potash and permanganate of potassa, and the quantity of ammonia formed by their action is taken as a measure of certain (albuminoïd) organic substances. The whole of the nitrogen present in organic combination is not obtained in this manner; more or less of the nitrogen in some organic substances being converted into products other than ammonia. By this treatment, it must as yet be considered an open question as to which of these methods will be of most service for testing the goodness of a potable water; it will be best, therefore, to describe the various methods in detail.

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[*] Chem. News. 36, 26.

[†] Landwirthschaftliche Versuchsstationen, 10, 516; Zeitschr. f. anal. Chem. 8, 494.

[‡] Zeitschr. f. anal. Chem. 8, 495.

[§] Comp. Wanklyn, Chapman, and Smith, Journ. Chem. Soc. 21, 152; also Kubel and Tiemann, *loc. cit.*, p. 98.

[||] Journ. f. prakt. Chem. [N. F.] 4, 364.

[¶] 1 gram grape sugar separates ·900 silver, 1 gram uric acid 1·285, 1 gram gallic acid 3·812.

[**] Journ. Chem. Soc. 20, 591.

A. Methods based on the reduction of permanganate of potassa.

This salt was used as a test for organic matter in water thirty years ago by FORCHHAMMER,* and subsequently by E. MONNIER.† Both these chemists warmed the water, and the latter acidified it before adding the permanganate. At present the method employed is somewhat different; excess of the permanganate is first added, then sulphuric acid, then standard oxalic acid until colourless, and finally permanganate again to incipient reddening. H. TROMMSDORFF,‡ who improved SCHULZE's earlier method, allows the permanganate to act first in alkaline, and afterwards in acid solution; whilst KUBEL (*loc. cit.* p. 104) employs an acid solution only. As the action is more energetic in alkaline than in acid solution, more is usually required in the SCHULZE-TROMMSDORFF process than in KUBEL's (other conditions being the same), but the differences are usually small (KUBEL and TIEMANN, *loc. cit.* p. 109).

The following is a description of the SCHULZE-TROMMSDORFF process, which is to be preferred on these grounds:—

α. Requisites.

a. Distilled water, which should have no appreciable action on permanganate of potassa. This may be obtained by adding to the water some crystallized permanganate and pure soda, distilling and rejecting the first quarter of the distillate, collecting the rest. No luting, indiarubber, or other organic substance, should be used at the joints of the apparatus. 100 c. c. of the water should not decolorize more than 1 c. c. of the permanganate solution *e*.

b. Solution of soda.—Caustic soda prepared from sodium is fused in a silver crucible, and when cold is dissolved in twice its weight of the pure water, *a*.

c. Dilute sulphuric acid.—Pure concentrated sulphuric acid is mixed with three times its volume of the pure water.

d. Centinormal oxalic acid.—The oxalic acid is purified by rapidly cooling a hot concentrated solution, and drying the thin needles at the ordinary temperature on filter paper: 0·63 gram of this is dissolved to 1 litre, or 10 c.c. of a normal oxalic acid solution may be diluted to 1 litre. This solution is capable of reducing 0·3163 gram permanganate of potassa, and should be kept in the dark in a stoppered bottle.

e. Solution of permanganate of potassa.—About 0·32 gram of crystallized permanganate of potassa is dissolved in 1 litre of the pure distilled water. To standardize it, 20 c. c. of the oxalic acid solution are warmed with 2 c. c. dilute sulphuric acid, to 60°, and the permanganate run in until a pale reddish colour is produced which is permanent

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* Institut, 1849, 383; Jahresber. v. LIEBIG u. KOPP, 1849, 603.

† Compt. rend. 50, 1084; DINGLER's polyt. Journ. 157, 132.

‡ Zeitschr. f. anal. Chem. 8, 344.

(p. 217, *cc*, Vol. I.), and from this result the permanganate is diluted if necessary, so that 20 c.c. may exactly decompose 20 c. c. of the oxalic acid solution: 1000 c. c. of the solution now contain 0·3163 gram of permanganate of potassa. The solution should be kept in the dark in a stoppered bottle and always be measured from a Gay-Lussac's burette, or, more conveniently, from a burette with glass tap.

β. The actual analysis.

100 c. c. of the water are placed in a flask holding about 300 c. c., half a c. c. of soda and 10 c. c. of permanganate are added, the whole boiled for ten minutes, and allowed to cool to 50 or 60°; 5 c. c. dilute sulphuric acid, and then 10 c. c. of centinormal oxalic acid are run in; as soon as the liquid is colourless, permanganate solution is carefully added drop by drop with shaking until the liquid has a faint permanent red tint. The permanganate employed for this purpose is the quantity required for the destruction of the organic matter in the 100 c. c. of the water.* Good spring water never requires more than 1—2 c.c. of the permanganate solution; if more than 4 c.c. are used, a second experiment must be made, using more permanganate and a corresponding quantity of soda; for the excess of permanganate remaining undecomposed after boiling must always be at least double the amount decomposed.

The results are reported as so much pure permanganate of potassa, or so much oxygen, required for the oxidation of the organic matter in a litre of the water. 1 c. c. of the solution contains + 0·0003163 gram of the permanganate or = 0·00008 gram of available oxygen.

B. Method founded on the reduction of oxide of silver.

H. Fleck,† who first proposed the use of nitrate of silver in alkaline solution for the comparative estimation of organic matter in water, claims for it, as an advantage over permanganate, that it oxidizes those substances only which may be expected to be injurious, whilst the permanganate oxidizes all organic substances alike when boiled with them in alkaline solution. The silver solution for instance is not reduced by the fatty acids or their salts, or by the acids of the lactic and succinic series, whilst it is reduced by the colouring matters of bile, and generally by animal and vegetable colouring matters, taurine, mucus, uric acid, tannic acid, gallic acid, dissolved proteids, grape sugar, and all volatile products of putrefaction. It will be noticed, however, that this list evidently includes many substances which would be quite harmless.

a. Requisites.

a. Alkaline silver solution.—17 grams of nitrate of silver are dissolved in about 50 c. c. water and the solution poured into a litre flask containing a solution of 48 grams soda and 50 grams hyposulphite of soda; the mixture is shaken, the flask filled to the mark, again shaken, poured into a larger flask, and boiled for a quarter of an hour; a little silver will separate, reduced by organic matter in the water, &c. After 24 hours the solution is poured off from the separated silver, and kept in the dark in a blackened bottle. In using it, a Gay-Lussac's or Geisler's burette should be employed, or one with a glass tap.

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* The result, however, is inaccurate if nitrites are present; in that case a correction must be applied. For every 5 eq. nitrous acid 2 eq. permanganate must be deducted, that is, for 1 part nitrous acid 1·66 parts solid permanganate. Ammonia also introduces error; it should be removed if in any notable quantity by boiling off a third of the water, the quantity being afterwards made up with distilled water. Of course small quantities of volatile organic matter may escape in the process.

† Journ. f. prakt. Chem. [N. F.] 4, 364.

b. Solution of iodide of potassium.—Dissolve $\frac{1}{20}$ eq. or 8·299 grams chemically pure salt dried at 180° to 1 litre. This solution will precipitate $\frac{1}{20}$ eq silver (5·3965 grams) from a solution of the nitrate.*

c. A small quantity of a freshly prepared mixture of dichromate of potassa solution, pure hydrochloric acid and starch paste in equal measures all of the ordinary strength.

β. The actual analysis.

In order to ascertain how much silver is reduced by the organic matter in 1 litre of water, three operations are necessary: (*a*) the estimation of the silver in the silver solution, (*b*) the treatment of the water with a known quantity of silver solution, (*c*) the estimation of the silver remaining in solution after the last experiment, which will give the amount of reduced silver.

a. 10 c. c. of the silver solution is measured into a beaker, 100 c. c. distilled water added, and iodide of potassium run in from a burette, until it is present in the smallest excess. This point is ascertained by testing—as soon as the separation of iodide of silver begins to decrease—a drop of the fluid with a drop of the chromic starch solution on a porcelain plate. The smallest excess of iodide of potassium is at once indicated by the appearance of a bluish tint; whilst the iodide of silver is not decomposed until after long contact of the two drops. If too much iodide of potassium has been used, a little more silver solution is added and the end reaction approached more cautiously.

b. 100 c. c. of the water are measured into a beaker, 10 c. c. silver added † and the whole boiled, when a white precipitate, consisting of lime and magnesia salts, is usually formed; this gradually becomes grey or black if any oxidizable organic matter is present. The boiling is continued for ten minutes or so until the precipitate settles quickly on removing the lamp. The water lost by evaporation is then replaced by distilled water, and it is allowed to cool.

c. When the fluid is cold, the dissolved silver is estimated as in *a*, without removing the precipitate. The difference of the c. c. iodide of potassium used in *a* and *c* expresses the precipitated silver; 1 c. c. = in round numbers 0·0054 silver. Multiplying the silver found by 10 gives silver reduced by 1 litre of the water.

C. Method depending on the conversion of the nitrogen of albuminoïd bodies into ammonia.

In this method, which was introduced by Wanklyn, Chapman, and Smith,‡ all the ammonia existing as such is expelled from the water by boiling it in a distilling apparatus with or without the addition of an alkali, and then the albuminoïd bodies present are decomposed by boiling with potash and permanganate of potassa, the ammonia thereby produced being distilled off and estimated. Two results are thus obtained, the ammonia present as such, and the ammonia produced from albuminoïd bodies.

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* Fleck estimated the iodide of potassium in solution by precipitating the iodine as iodide of silver (§ 145, 1, *a*, *a*, Vol. I.).

† If a precipitate appears at once, it may be either sulphide of silver, or metallic silver, the former would indicate sulphuretted hydrogen or dissolved sulphides, the latter salts of protoxide of iron (or protoxide of tin, possibly).

‡ Journ. Chem. Soc. 20, 591; also Water Analysis, by Wanklyn and Chapman, 3rd edition, 1874.

a. Requisites.

a. Nessler test.—Prepared by boiling together 35 grams iodide of potassium, 13 grams mercuric chloride and 800 c. c. water. When the solution is clear, a cold saturated solution of mercuric chloride is added drop by drop until the precipitate just begins to be permanent. 160 grams hydrate of potassa or 120 grams hydrate of soda are now added, the solution made up to 1 litre, a little more mercuric chloride solution is added, and the mixture is allowed to settle. The clear liquid has a slightly yellowish tinge. 2 c. c. added to 50 c. c. water containing 0·05 mgrm. ammonia should immediately give a yellowish brown coloration. The solution should be kept in a well-stoppered bottle. In using it, some is poured into a small bottle.

b. Standard solutions of chloride of ammonium.—For the stronger solution, 3·15 grams of chloride of ammonium is dissolved to 1 litre, 1 c. c. = 1 mgrm. NH_3. The weaker solution of one-hundredth the strength is prepared by diluting 10 c. c. to 1 litre : 1 c. c. = 0·01 mgrm. NH_3.

c. Alkaline solution of permanganate of potassa.—100 grams of caustic potash and 4 grams of crystallized permanganate of potash are dissolved in 500 c. c. water, boiled for 15 minutes, poured into a 500 c. c. flask, and made up to the mark when cold.

d. Freshly ignited carbonate of soda, or a solution of the salt freed from all traces of ammonia by boiling.

e. Distilled water free from ammonia.—If the distilled water in general use is coloured when 50 c. c. is tested with 2 c. c. Nessler test, some must be prepared specially by adding a trace of dilute sulphuric acid to the water and distilling.

f. A stoppered retort, holding somewhat more than a litre when quite full. This is held in a strong retort-holder and heated directly by a large lamp, preferably a Maste's (fig. 47, p. 60, Vol. I.).

g. A large Liebig's condenser. Length of internal tube 90 cm., width, 3 cm. The neck of the retort is bound round with a narrow strip of writing-paper and inserted directly into the condenser.

h. Six cylinders of white glass, about 17 cm. high and 4 cm. wide. These, when in use, are placed on a white porcelain plate or a sheet of white paper.

i. Measuring vessels, namely, a half-litre flask to measure the water, a cylinder with a mark at 50 c. c. for the alkaline solution of permanganate, a burette for the chloride of ammonium, and a 2 c. c. pipette for the Nessler test.

As all vessels kept in a laboratory usually have traces of ammonium salts on their surface, care must be taken to rinse them with pure water before use; and, in fact, the most scrupulous cleanliness must be observed throughout the operation.

β. The actual analysis.

a. The retort and condenser being arranged, 500 c. c. of the water are poured into the retort and heated over the naked flame.* The lamp is moved backwards and forwards at first under the retort, and the drops of water which condense on its surface are wiped off with a cloth: the contents of the retort very soon begin to boil. The distillate is collected in one of the cylinders. As soon as 50 c. c. have run over, the cylinder is changed, the first being put aside for testing, and the distillation is continued until 150 c. c. more have passed over. The retort will now contain 300 c. c. The lamp for a moment is removed, 50 c. c. of the alkaline solution of permanganate are poured into the retort through a wide-necked funnel, and the distillation is again set going. If bumping seems likely to occur, it may be obviated by gently shaking the contents in the retort. 150 c. c. more are now distilled over, collecting the distillate of three cylinders, 50 c. c. in each cylinder. These are reserved for testing, and the distillation is stopped.

b. The small quantities of ammonia in the four reserved cylinders have now to be estimated by the Nessler test.†

For this purpose, 2 c. c. of the Nessler test is put into the first cylinder by means of the 2 c. c. pipette, and stirred. If ammonia is present, a yellowish-brown colour will be produced, varying in depth according to the quantity of ammonia. This colour has now to be imitated by measuring a known quantity of the weaker chloride of ammonium solution into another cylinder, filling it up to 50 c. c., adding 2 c. c. Nessler test, and stirring. After a few minutes, the colours of the liquid in the two cylinders standing side by side on a white surface, are compared by looking down through the liquid. If the colours are not alike, another trial must be made, using more or less chloride of ammonium solution as the case may be, until the two solutions are of exactly the same tint. When this is the case, the quantity of ammonia present in the first cylinder is considered to be the same as that containing the known quantity of chloride of ammonium.

Chloride of ammonium must never be added to the liquid after the Nessler test, as this would cause turbidity, and the two solutions could not be compared. Moreover, comparisons cannot be made between liquids unless they have the same (mean) temperature,‡ and unless the quantity of ammonia in 50 c. c. lies between 0·0025 and 0·05 mgrm.

The ammonia in the first cylinder was present in the water as such, that is, in the form of an ammonium salt. In accordance with the results of numerous experiments by the authors, it is usual to add one-third to the amount of ammonia here found, in order to obtain the total free ammonia present as such in the half litre of water, thus saving the trouble of Nesslerizing the 150 c. c. drawn over before the permanganate is added. The contents of the other three cylinders are separately Nesslerized in a similar manner. The sum of the results represents the ammonia produced by the action of alkali and permanganate of potash on the nitrogenous matter. The authors called the ammonia first given off *free ammonia*, that given off after addition of permanganate *albuminoïd ammonia*.

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* If the water is acid some freshly ignited carbonate of soda must be added before heating it, to set free the ammonia. This addition is not necessary for ordinary waters containing, as they usually do, alkaline earthy carbonates.

† This process was first recommended by W. A. Miller.

‡ Nessler, Zeitschr. f. anal. Chem. 7, 415.

12. Estimation of Ammonia.

Great importance is justly attached to this determination of ammonium compounds in natural waters, for the presence of any considerable quantity would generally indicate that it was contaminated with substances formed by the putrefaction of nitrogenous organic matter, and that they had not been sufficiently removed by the action of air and filtration through the ground.

Many methods are in use, the most important of which will be described.

a. Expulsion of the ammonia by distillation and conversion into platino-chloride of ammonium.—This method is often employed for mineral waters, and will be described in § 209.

b. Expulsion of the ammonia by distillation and Nesslerizing. (See pp. 128 and 129).—This is convenient when very small quantities of ammonia have to be estimated.

c. Direct Nesslerizing, after precipitation of lime, &c.—This method, distinguished for its extreme simplicity, is sufficient in most cases, and must be considered as a decided improvement on WANKLYN and CHAPMAN'S* original method. It was introduced by FRANKLAND and ARMSTRONG,† and improved by H. TROMMSDORFF.‡

300 c. c. of the water are put into a stoppered cylinder with 2 c. c. of solution of carbonate of soda (one part of the salt to two of water), and 1 c. c. of solution of hydrate of soda (one soda to two of water), the cylinder is closed, shaken, and allowed to settle. 100 c. c. may generally be poured off clear, if not this quantity must be filtered off through a washed filter. The clear liquid is poured into a cylinder or test glass, with a mark on the side, and 1 c. c. Nessler test added (*a*, p. 128); if the colour produced is more than yellow, 1 c. c. more is added. Into a second cylinder or test glass, precisely similar to the first, 90 c. c. pure distilled water (*e*, p. 128) is put, together with 0·6 c. c. carbonate of soda solution, and 0·3 c. c. soda solution; it is then filled to the mark, and a certain quantity of the weaker chloride of ammonium solution (*b*, p. 128) run in from a 1 c. c. pipette divided into hundredths, adding 1 or 2 c. c. of the Nessler test according to circumstances. After it has been shaken it is allowed to remain a few minutes, and the colours in the two cylinders or test glasses are compared, the method prescribed on p. 129 being accurately followed. From what is there stated, it is evident that if the Nessler test produces too dark a colour in the first trial, a fresh quantity of the clarified water must be taken, diluted with the proper proportion of pure distilled water to 100 c. c., and tested again.

d. Precipitation of the ammonia by iodide of mercury and potassium, and the estimation of the mercury in the precipitate (FLECK§).—This is particularly suitable when the ammonia is present in comparatively large quantity: it is therefore supplementary to *b* and *c*, which are suited to waters poor in ammonia, the process consists in precipitating the ammonia by Nessler test as $NHg_4I + 2HO$, an insoluble compound of constant composition. In order to be able to filter this well, it must be precipitated in conjunction with carbonate of lime or hydrate of magnesia; some solution of sulphate of magnesia is therefore added to the water. The mercury is estimated by dissolving the iodide of tetramercurammonium in hyposulphite of soda solution and titrating with alkaline sulphide, 4 eq. (400) mercury correspond with 1 eq. (17·04) ammonia.

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* Journ. Chem. Soc. 21, 161.

† *Ib.* 21, 77.

‡ Zeitschr. f. anal. Chem. 8, 356.

§ Journ. f. prakt. Chem. (N. F.) 5, 263.

The following reagents are required:—

Nessler test (p. 128).
Solution of sulphate of magnesia (1 to 8).
Solution of hyposulphite of soda (1 to 8).
Standard solution of alkaline sulphide.
Acetate of lead paper. Made by dipping filtering paper into acetate of lead solution (1 to 10) and drying. It must be kept in a well-closed bottle.

The alkaline sulphide solution is made by heating 10 grams carbonate of potassa and soda with 4 grams sulphur in a covered porcelain crucible to calm fusion, dissolving the sulphide, when cold, in water, adding 10 grams soda, and diluting to 1 litre. The solution will keep unchanged for a week in a well-closed bottle. It is titrated with a standard solution of chloride of mercury, containing, say, 1 gram of the chloride in 100 c. c. 10 c. c. of this is decomposed with carbonate of ammonia, the white precipitate dissolved in a few drops of hyposulphite of soda, and the sulphide solution run in from the burette. A black precipitate of sulphide of mercury will be formed which is flocculent at first and afterwards granular. As soon as the liquid begins to get clear the reagent is to be cautiously added drop by drop until a faint brown ring is formed when a drop of the liquid is placed on the lead paper. 100 c. c. of the sulphide solution should precipitate about 0·5 gram mercury. If necessary it should be diluted to this strength.

Everything being prepared, 200 c. c. of the water is mixed in a cylinder with 0·5 c. c. of sulphate of magnesia solution, 4 c. c. Nessler test added, the cylinder closed, shaken and allowed to settle. If the precipitate is not red, but only yellow from the quantity of ammonia being too small, the experiment must be repeated with 500 c. c. water or more, using proportional quantities of sulphate of magnesia and Nessler test. When the precipitate has thoroughly settled, the clear liquid is poured off as closely as possible, the precipitate transferred to a filter and washed with cold water, until the washings cease to be alkaline. This operation must of course be carried out in an atmosphere entirely free from sulphuretted hydrogen and ammonia. The filter is now completely filled with hyposulphite of soda solution which will dissolve the mercurial salt, it is washed with cold water, and the mercury in the solution (amounting to, say, 100 or 150 c. c.) titrated as above.

In testing the methods *b*, *c*, *d*, Kubel and Tiemann (loc. cit. p. 97) obtained on the whole sufficiently accurate and tolerably concordant results.

II. The Water is not Clear.

1. A large bottle of known capacity is filled with the water, closed with a glass stopper, and allowed to settle in the cold; the clear water is drawn off with a siphon as far as practicable, and the deposit collected on a filter and weighed after drying or ignition. The clear water is treated as directed in I.

2. Another stoppered bottle is filled with the water and allowed to

stand in the dark. As soon as this has settled, the clear water is drawn off very cautiously with a siphon so as not to disturb the deposit: the latter is shaken up with the remainder of the water, poured into a small beaker, which is covered, and allowed to remain at rest until the deposit has settled again. The water is then poured off as closely as possible, some of the deposit sucked up with a glass tube, drawn out to a capillary point, and examined under a microscope for organized bodies (bacteria, infusoria, &c.).

For the calculation of the analysis, the reader is referred to § 213; it should be observed that the results are *usually* arranged on the following principles:*—

The *chlorine* is combined first with sodium; if there is an excess (which rarely occurs) this is combined with calcium. The *sulphuric acid* is combined first with lime. The *nitric acid* is combined first with ammonia, and the remainder, if any, with soda, if the latter has not been used up for the chlorine, otherwise with magnesia. The *silicic acid* is put down in the free state, the remainder of the lime and magnesia as carbonates, usually as neutral carbonates.

It must always be borne in mind that the results of the qualitative analysis may render another arrangement of the acids and bases necessary. For instance, if the evaporated water is strongly alkaline, carbonate of soda is present, generally along with sulphate of soda and chloride of sodium, sometimes also with nitrate of soda. The lime and magnesia should then be entirely combined with carbonic acid.

In the report, the quantities are represented in parts per 1000 by weight, or—what comes to the same thing in potable water—in grams per litre (or sometimes in grains per gallon of 70,000 grains). KUBEL and TIEMANN recommend exhibiting the results in parts per 100,000, but the adoption of the gram and the litre presents the advantage of using terms to which all who are accustomed to weigh and measure attach definite ideas.

APPENDIX.

ESTIMATION OF HARDNESS.

It is sometimes sufficient for technical purposes merely to estimate the so-called *hardness* of a water. By hardness is understood the quality communicated to a water by the presence of lime and magnesia salts; a hard water being one which is rich in these salts, whilst a soft water contains but little of them. The *total hardness* is that of the water in its natural state; the *permanent hardness* is that retained by the water after being boiled and made up to its original volume with distilled water; the *temporary hardness* is the difference between the two.

The total hardness, both permanent and temporary, may be obviously calculated from the results of the analysis. CLARK,† however, proposed a more rapid way of attaining this object. His process has been altered in many ways, but the re-agent which he employed, *soap solution*, is still always used. The soap decomposes the lime and magnesia salts present, and a slight excess of soap can be easily recognised by its giving a permanent lather when the water is shaken: but as this test does not distinguish between lime and magnesia, the results are quite different from those obtained by actual analysis, and require some conventional method of expression. Unfortunately, this method varies in different countries, being different in Germany from what it is in France or England, as seen below:—

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* A certain latitude is here allowed to the analyst's discretion.

† Jahresber. f. Chem. 1850, 608; and "On the Examination of Water for Towns for its Hardness" &c., by T. CLARK, London, 1847.

Value of a Degree of Hardness.

In Germany . . .	1 part CaO in 100,000 parts of water, or 1 mgrm. CaO in 100 c. c.
In France	1 part CaO,CO_2 in 100,000 parts of water.
In England . . .	1 part CaO,CO_2 in 70,000 parts of water. Or 1 grain CaO,CO_2 in a gallon.

The various degrees, therefore, stands to each other thus:

German.		French.		English.
0·56	:	1	:	0·70

So that to convert German degrees into French multiply by 1·7857, into English by 1·25, and conversely to convert English degrees into French multiply by 1·4286, into German by 0·8.

According to comparative experiments made by Kubel and Tiemann, the best method in general is Clark's, as modified by A. Faiszt and C. Knausz,* it must be observed, however, that the methods proposed by Boutron and Boudet† and by Wilson‡ have certain advantages. The first method only, will be described here.

a. Requisites.

a. Standard solution of chloride of barium.—0·523 gram of pure dry crystallized chloride of barium (BaCl, 2 aq.) as dissolved (equivalent to 0·120 gram lime) to 1 litre; so that 100 c. c. contain chloride of barium equivalent to 12 mgrm. lime, we have a solution of 12° hardness (German).

b. A stoppered bottle, holding about 200 c. c. with a mark at 100 c. c.

c. Standard soap solution.—To prepare the soap, 150 parts of lead plaster are warmed on a water-bath with 40 parts of pure carbonate of potassa, and rubbed down to a uniform consistence; it is then treated with strong alcohol, allowed to deposit, and filtered. The spirit is distilled off, and the residual soap dried in the water-bath (H. Trommsdorff§). 20 parts of the potash soap prepared in this way are dissolved in 1000 parts spirit of 0·9213 sp. gr.: 100 c. c. of the standard chloride of barium is transferred to the stoppered bottle (*b*) and the soap solution run in from the burette, until a thick white froth is produced on shaking; this lather must remain on the surface for at least five minutes. The soap should be added at first in larger quantities, then drop by drop, shaking after each addition. The bottle should be upright and shaken up and down.

If the soap solution has been prepared in the manner described above, less than 45 c. c. will suffice for 100 c. c. chloride of barium solution. To make sure of the result the experiment is repeated, and then the soap solution is diluted with spirit of the above gravity, so that 45 c. c. may first produce the froth in 100 c. c. of the chloride of barium solution.

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* Gewerbeblatt aus Würtemberg, 1852, 193; Chemisch-pharmaceut. Centralbl, 1852, 513.

† Chem. Centr. 1855, 343.

‡ Annal. d. Chem. und Pharm, 119, 318.

§ Zeitschr. f. anal. Chem. 8, 333.

d. The following *table* constructed by **Faiszt** and **Knausz** from direct experiments:—

c.c. of soap solution used.	Degrees of hardness.	Degree of hardness corresponding to 1 c.c. soap.
3·4	·5	·25
5·4	1·0	
7·4	1·5	
9·4	2·0	
11·3	2·5	·26
13·2	3·0	
15·1	3·5	
17·0	4·0	
18·9	4·5	
20·8	5·0	
22·6	5·5	·277
24·4	6·0	
26·2	6·5	
28·0	7·0	
29·8	7·5	
31·6	8·0	
33·3	8·5	·294
35·0	9·0	
36·7	9·5	
38·4	10·0	
40·1	10·5	
41·8	11·0	
43·4	11·5	·31
45·0	12·0	

The necessity for this table is evident, for on looking at it, it will be seen that the proportion between the soap used and the degree of hardness is not constant.

β. The Actual Determination.

aa. Estimation of total hardness.

For a preliminary test, 20 c. c. of the water are put into a test tube, 6 c. c. soap solution added and the mixture shaken, it will then be seen whether an opalescence, a slight or a marked turbidity, or a notable precipitate is produced. This result gives an indication as to the quantity of water to be taken for the actual determination. If the water is very soft, 100 c. c. are put into the stoppered bottle; if moderately soft, 50 c. c. and 50 c. c. distilled water are taken; if moderately hard, 20 c. c. and 80 distilled water; if hard, 10 c. c. and 90 of distilled water. If a frothy pellicle is formed on the surface of the fluid in the preliminary test, magnesia salts are present in considerable quantity and it will be absolutely necessary to dilute the water largely. The soap solution is now run from the burette into the stoppered bottle, shaking after each addition, and finishing as soon as the characteristic froth is produced and is permanent. In the first experiment, the soap solution should be added in larger portions to begin with, and afterwards 1 c. c. at a time. In the second experiment nearly the required quantity is run in at once, and then the soap solution is added drop by drop. The concentration of the water may be taken as correct if from 20 to 45 c. c. soap have been used. The soap used must never exceed 45 c. c.

Having read off the number of c. c. of soap used (n), the degree of hardness (*of the water as tested in the bottle*) is found by the table as follows: If n is identical with a number in the first column, say 22·6, the degree of hardness can he found at once in the second column, which in this case will be 5·5. If n is not to be found in the first column, the next lower number (l) in the column is noted, and the degree of hardness corresponding to it is written down. l is now deducted from n, the difference multiplied by the proper number in the third column, and the product added to the degree of hardness first written down. An example will make this clear. Suppose that 100 c. c. of the water has taken 43·6 c. c. soap solution

$$\begin{array}{ll} 43{\cdot}4 \text{ c. c.} \ldots\ldots\ldots & 11{\cdot}5^\circ \text{ hardness} \\ (43{\cdot}6 - 43{\cdot}4) \times 0{\cdot}31 \ldots\ldots & = 0{\cdot}062 \\ \hline & 11{\cdot}562 \end{array}$$

If the water as tested in the bottle has been diluted, the degree thus found must be increased in the proper proportion.

bb. Estimation of permanent hardness.

500 c. c. of the water is boiled in a flask holding about a litre for half an hour to an hour, the water as it evaporates being replaced by adding distilled water from time to time. When cold it is transferred to a half-litre flask, rinsing out with small quantities of distilled water; the flask is then filled up to the mark with distilled water, shaken, allowed to deposit, the water filtered into a dry bottle, and the hardness determined exactly as above.

b. ANALYSIS OF MINERAL WATERS.*

§ 206.

Here a larger number of substances claims our attention than in the analysis of fresh waters. The following substances may be present:—

a. Bases: Potassa, soda, lithia, oxide of cæsium, oxide of rubidium, ammonia, lime, baryta, strontia, magnesia, alumina, protoxide of iron, protoxide of manganese (oxide of zinc, protoxide of nickel, protoxide of cobalt, oxide of copper, oxide of lead, teroxide of antimony, and sometimes also oxides of other heavy metals).

b. Acids, &c.: Sulphuric acid, phosphoric acid, silicic acid, carbonic acid, boric acid, nitric acid, nitrous acid, hyposulphurous acid, chlorine, bromine, iodine, fluorine, sulphuretted hydrogen, crenic acid, apocrenic acid, formic acid, propionic acid, &c. (arsenious and arsenic acids, titanic acid).

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* Compare Qualitative Analysis, § 211.

c. *Non-combined elements and indifferent gases:* Oxygen, nitrogen, light carbide of hydrogen.

d. *Indifferent organic matters.*

Many of these substances usually occur in springs in considerable proportions; more particularly soda, lime, magnesia, and sometimes also protoxide of iron; also sulphuric acid, carbonic acid, silicic acid, chlorine, and sometimes also sulphuretted hydrogen. The others are almost invariably found in smaller quantity and often in exceedingly minute proportions. The substances between brackets are usually to be detected only in the residue from the evaporation of large quantities of water, or in the muddy ochreous-deposits, or solid sinter-deposits, which form, in most mineral springs, in the parts where the air acts on the water flowing off, or kept in a reservoir.*

The subject of the analysis of mineral waters is properly treated under two heads, viz., 1. *The analytical process:* and, 2. *The calculation and arrangement of the results.*

1. The Analytical Process.

The performance of the analytical process is divided into two parts, viz., 1, operations at the spring or well; and, 2, operations in the laboratory.

A. Operations at the Spring or Well.

I. Apparatus and other Requisites.

§ 207.

1. A common plunging siphon of 200—250 c. c. capacity.

2. Four flasks of about 300 c. c. capacity. Each contains about 3 grams hydrate of lime quite free from carbonic acid, or containing a known quantity of carbonic acid (Vol. I. p. 331), and—if the mineral water contains carbonate of soda—about 1·5 gram dry chloride of calcium. Each flask is weighed with the hydrate of lime, &c., and its caoutchouc stopper, and the weight is marked on a label gummed on the flask. The size of the neck must be about the same in all the flasks, so that *a single cork* with its tubes, as in Fig. 80, p. 141, may fit all the flasks; this should be prepared beforehand.

3. An accurate thermometer with very distinct scale.

4. About eight white glass bottles of 2 to 3 litres capacity, provided with well-fitting glass stoppers.

5. Four white glass bottles, holding about 7 litres, provided with accurately fitting glass stoppers.

6. A clean carboy in basket, provided with caoutchouc stopper; this should be rinsed out with distilled water.

7. A litre and a half-litre flask.

8. One middle-sized and two large funnels.

9. Swedish filtering paper.

10. Flasks, beakers, lamp, blow-pipe, glass rods, glass tubes, caoutchouc tubing, files, scissors, knife, caoutchouc stoppers, corks, string, &c.

11. Reagents, more especially the following: ammonia, hydrochloric

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* As I have already mentioned in the Qualitative Analysis, if oxide of lead, oxide of copper, oxide of tin, &c., are found, it must be a subject of careful examination whether these oxides really proceed from the water or from any metallic pipes, cocks, &c.

acid, acetic acid, nitrate of silver, chloride of barium, oxalate of ammonia, tannic acid and gallic acid (or infusion of galls), tincture of litmus (freshly prepared), and test papers.

Besides these articles, the following are also required under certain circumstances:—

a. When the Water contains Sulphuretted Hydrogen or an Alkaline Sulphide.

12. A standard solution of iodine in iodide of potassium. This must be very dilute, say 1 c. c. = about 0·001 gram iodine. Such a solution may be prepared by mixing one volume of BUNSEN's solution of iodine (§ 146 *b*, γ) with four volumes of water.

13. Starch-powder.

14. A Mohr's burette, and several pipettes.

15. A solution of arsenious acid in hydrochloric acid, or of arsenite of soda, or of acetate of copper; also the reagents and apparatus mentioned p. 142 of this volume.

b. When the Water contains much Protoxide of Iron, which it is intended to estimate directly (volumetrically) at the Spring or Well.

16. Burettes, pipettes, and a solution of permanganate of potassa. For waters containing much iron, this solution must be diluted so that 100 c. c. of it will convert about 0·1 gram of iron from the state of protoxide to that of sesquioxide. If the water contains only a moderate proportion of iron, the solution must be still more diluted. If the solution has to be standardized on the spot, weighed pieces of pianoforte wire, or a standard solution of oxalic acid (Vol. I. p. 217) will be also required.

c. When the whole of the Gases dissolved in the Water are to be determined.

According as the water is poor or rich in carbonic acid, the method § 208, 10, *a* or *b*, is employed.

17. The apparatus there described will then be required.

d. When the free Gases which are evolved at the Spring have to be determined.

18. The apparatus described § 208, 11 will be necessary.

e. When the Well is deep, and specimens from various Depths are to be examined.

19. The apparatus figured p. 140 of this volume will be required.

f. If the Specific Gravity of highly Aërated Water is to be determined.

Under these circumstances,

20. One, or rather several bottles, such as are figured and described § 208, 13, must be provided.

II. Analytical Processes.

§ 208.

1. The *appearance* (colour, clearness, &c.) of the water is examined. A water will often look clear at a first glance, whilst on closer inspection in a large white bottle will show a few, or even a great many, coloured or colourless flakes, &c. In such cases, the bottle is allowed to stand a

day in a cool place, the clear water then siphoned off, and the matters which may have subsided are examined under the microscope. This examination often reveals the presence of infusoria, plants of the lowest order, &c.*

2. It should be noted whether there is disengagement of *gas* at the well, or whether the water forms small pearly bubbles when poured into a dry glass, or whether gas is disengaged when the water is shaken in a half-filled bottle.

3. The *taste* and *smell* of the water must be noted. To detect very minute portions of odorous matters, a water bottle is half filled with the water, covered with the hand, and vigorously shaken; on taking off the hand, any odour is readily perceptible.

4. The *reaction* of the water is ascertained by testing with different test papers (or, better still, with blue and but very slightly reddened tincture of litmus); it must be noted also whether the colour which the paper has acquired changes when it is dried in the air.

5. The *temperature* of the water is examined. If practicable, the simplest and best way is to plunge the thermometer into the spring, and to note accurately the height of the mercury whilst the thermometer is still in the water; or a large bottle with a thermometer in it is filled with water by immersion in the spring, and left some time in the latter; it is then taken out, and the temperature accurately ascertained by reading the thermometer in the bottle. If the water flows from a pipe, it is received in a large glass funnel which has the neck contracted so that it will allow about as much water to run out as enters. The thermometer is fixed in the middle of the water in the funnel, and read off after some time.

In addition to the temperature of the spring, note must be also taken of—

a. The date.

b. The temperature of the air.

c. The circumstance whether the temperature of the water is constant, or varies in the different seasons of the year; this may generally be ascertained on the spot.

6. *The bottles specified in* § 207, 4 *and* 5, *and the carboy are filled with water.* In doing this, great care must be taken to prevent the water from becoming turbid, which is very likely to happen if the bottle accidentally grazes the bottom or sides of the basin. If the water cannot be procured quite clear, it must be filtered into 4 of the 8 smaller bottles and into the larger bottles, using for this purpose large plaited filters of good filtering paper, so that the filtration may be very rapid. Very often the filtration may be avoided by filling the 6—7 litre bottles with the water, allowing them to stand quietly one to two hours in the shade, and then, when the flocks have perfectly settled to the bottom, drawing off the clear water into other bottles by means of a siphon. The bottles are closed securely and marked.

As impurities occasionally float on the surface of the water, it is always advisable to submerge the bottles entirely, and to a sufficient depth. In cases where it is desirable to avoid any agitation of the water in the well, the bottle or flask should be provided with the contrivance illustrated in Fig. 77.

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* Compare SCHULZ, Jahrbuch des Vereins für Naturkunde im Herzogthume Nassau, Heft viii. S. 49.

As soon as the thumb is raised, the water rushes into the vessel, whilst the air escapes through the other tube, which opens above the surface of the water. If the water lies out of reach, the bottle or flask is tied to a rod, or let down into the well suspended by a string, and with a weight attached. To keep the bottle or flask in an upright position, a net may be used, with a hole in the middle, through which the neck of the bottle is thrust, the net being then gathered and tied under the bottom, a sufficiently heavy weight fastened to it, and a strong string attached to the neck of the bottle.

If there is a deep well, and it is desired to take specimens of the water from various depths, the apparatus, fig. 78, may be used with advantage.

The strong flask *a* has a brass cap *b*, cemented air-tight on to the mouth, furnished with two brass tubes, *c* and *d*. A glass tube, *e*, is joined to *c*, and forms a downward continuation of it, reaching nearly to the bottom of the flask. The tube *d* descends *just* to the interior of the cap and surrounds the glass tube, as shown at *v*, fig. 79. The brass tubes are provided with cocks, *f* and *u*, which can be opened and shut with ease by the arms, *g* and *h*, and when open offer a perfectly free passage. If the cocks are to be turned simultaneously, as is usually the case, the ends of the arms are joined by *i* and *k*. In the position indicated by the figure, both cocks are closed; when *i* is drawn up, both are open. To prevent any mistake as to when the cocks are turned on or off, the ends of the arms should be marked. The upward continuations, *e′* and *m*, of the tubes fit air-tight on to the taps, being fastened by the screws *n* and *o*. The flask is surrounded with a silk net, to which are attached the weight *p* below, and the knotted cord *q* above; the latter serving to hold the apparatus during immersion and, at the same time, to measure the depth by the knots. The cord *r* is connected with *k*, the cord *s* with *i*; the upper ends of these cords are fastened to wooden rollers, which are marked to avoid confusion.

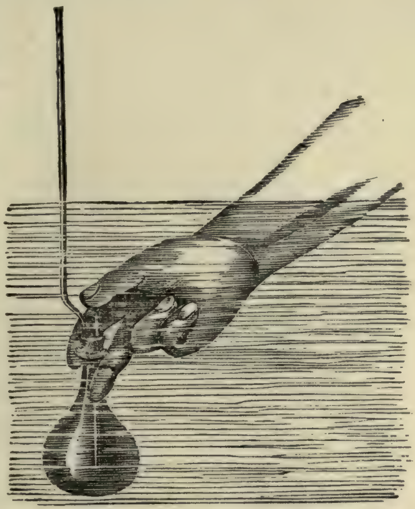
Fig. 77.

When the apparatus is to be used, the taps are closed, and it is allowed to sink to the desired depth, while two assistants, *R* and *S*, hold the cords *r* and *s* loosely, taking care, however, that the flask does not revolve on its axis, or the cords might become twisted. When the apparatus has been immersed some time, and the water has become still again, *S* draws up the cord *s*, and *R* loosens his hold of *r*. The cocks are thus turned on, and the water enters the flask through *e′ e*, while the air, passing out, escapes through the crescent-shaped opening at the top at *m*. The air ascends in large bubbles, which cease to appear when the flask is full; *R* now pulls *r*, while *S* slackens *s*.

The cocks being now closed, the apparatus is drawn up by *q*, whilst *R* and *S* gather in their respective cords gently. If the apparatus is properly constructed, the flask will now be quite full, and no bubbles will be visible on inverting it. To empty it, the apparatus is inverted, a bottle is placed under *m*, and the cocks are opened.*

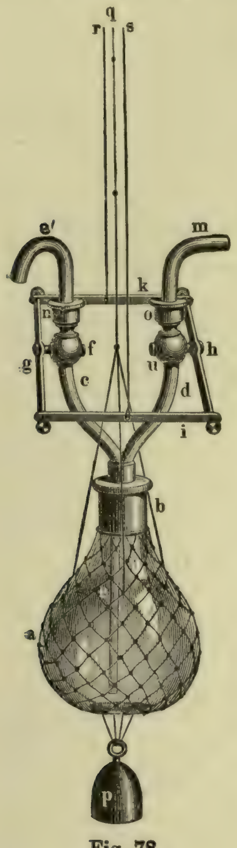

Fig. 78.

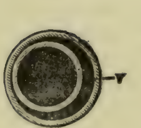

Fig. 79.

7. *To determine the total carbonic acid.*† Each of the weighed flasks containing hydrate of lime or hydrate of lime and chloride of calcium is filled to the neck with the freshly drawn water, gently shaking them round. If the flask can be plunged into the well, the cork with the two glass tubes (fig. 80) is put into the flask, and it is immersed so that the water flows in through *a b*, whilst the air escapes by *c d*. If, however, the spring rises by a narrow bore-hole so that the flask cannot be plunged into it, the siphon is rinsed out with some of the water and then gradually immersed, so that it fills slowly. It is then drawn out, wiped quickly on the outside, and emptied into the weighed flasks (§ 207, 2).

If the mineral water flows from a pipe, the weighed flasks containing hydrate of lime, &c., are held immediately under the stream, but not so close that the carbonic acid, which often (without being absorbed by the water) flows out along with it, can get into the flask. When filled, the flasks are tightly corked with the caoutchouc stoppers and tied down with parchment paper.

If the carbonic acid is to be determined in water collected by means of the apparatus, fig. 78, from the bottom of a well, and possibly supersaturated with carbonic acid, the safest course is to use the whole amount of the water contained in the flask *a*. In this case it is best to proceed as follows:—An excess of hydrate of lime free from carbonic acid (or a weighed quantity of hydrate of lime containing a known quantity of carbonic acid) and, if required, also a quantity of solid chloride of calcium more than sufficient to decompose the carbonate of soda, is put into a flask holding half as much again as *a*. The apparatus is then raised, the connectors *i* and *k* unscrewed (so that the taps may be opened separately), and also the top joints of the tubes, *m* and *e′*, and the small quantities of liquid which are above the taps, removed: the apparatus having been inverted obliquely, with the cock *u* in the lowest position and over the mouth of the flask, *u* is opened, and then the tap *f* cautiously. In this way the water passes out through *u*, while air enters through *f*. As soon as about $\frac{1}{4}$ of the contents has run out, the taps are closed, the stopper inserted in the flask, which is gently agitated so as to shake the hydrate of lime about, and thus effect the absorption of any carbonic acid that may have been disengaged from the water in pouring it in and have passed into the flask. The rest of the water is transferred to the lime-flask in the same manner. In order that the carbonic acid remaining behind in *a* may not be lost, about 50 c. c. lime-water or very thin milk of lime are poured into *a*, shaken for some time, and then emptied into the lime-flask, into which also *a* is to be rinsed; it is then corked and the cork fastened down.

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* The apparatus used by the Author has the following dimensions:—Capacity of the flask 600 c. c., internal diameter, of the brass tubes 7 mm., bore of the cocks 5 mm., length of the arms 90 mm., length of the lateral connectors of the arms 105 mm., weight of *p* 12·5 kilos.

† With respect to other methods of estimating carbonic acid, comp. § 139, I., *b*. *β*. The method described in the text is exceedingly simple, and surpasses all other methods in exactness (Zeitschr. f. anal. Chem. 2, 56).

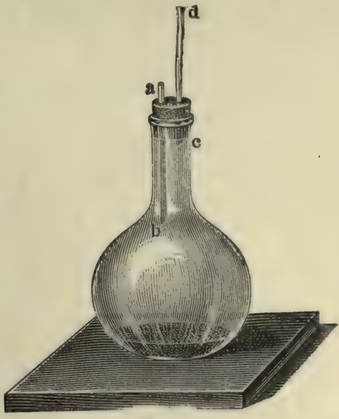

Fig. 80.

The capacity of *a*, and consequently the amount of water employed in this experiment, may be determined by measuring, but it is simplest, and saves all calculation, to refill the apparatus, as described, with the mineral water, to empty it into a tared flask, and weigh.

As the amount of free carbonic acid dissolved in a water varies with the pressure, it is necessary to note the height of the barometer.

8. *If the water contains sulphuretted hydrogen*, it is determined by standard solution of iodine (§ 207, 12), in the manner directed § 148, I. *a*. If the water contains an alkaline hyposulphite, it is of course necessary to deduct the amount of iodine corresponding with the hyposulphurous acid (determined separately) from the total, in order to ascertain how much has to be allotted to the sulphuretted hydrogen. If a gravimetric control is desired, the method with copper solution or arsenious acid solution may be employed (§ 148, I. *c*).

In the analysis of alkaline mineral waters, the question arises, how much of the sulphur compound found should be calculated as sulphuretted hydrogen, and how much as metallic sulphide or hydrosulphuretted sulphide? It is of importance, therefore, to know whether the water will lose part or the whole of its sulphur if a current of some indifferent gas is passed through it for a considerable time. For this purpose, a stream of hydrogen purified by passing it first through a concentrated alkaline solution of permanganate of potassa, and then through caustic potash, is allowed to bubble through a measured quantity of the mineral water in a flask furnished with a cork having two perforations. In one is fitted a tube reaching to the bottom of the flask, through which the gas enters, the other serves for the exit tube, which is bent at a right angle, and should not project through the cork. As soon as the issuing gas is quite free from sulphuretted hydrogen, and no longer decolorises a small quantity of solution of iodide of starch (which only occurs after the gas has been passing for some hours), the current of hydrogen gas is stopped, and the sulphur remaining in the mineral water thus treated is determined by means of iodine solution or copper solution, or a solution of arsenious acid. The operation should be conducted in a cool and shady place. By the simultaneous use of an air pump, the removal of the absorbed sulphuretted hydrogen is greatly facilitated.

The sulphur compound remaining in solution in the water in the flask is, in the case of mineral waters containing also free sulphuretted hydrogen, hydrosulphuretted sulphide. Although this method of deciding the question, which is recommended also by W. B. and R. E. ROGERS,* is well adapted for waters containing free sulphuretted hydrogen alone or almost exclusively, and no hyposulphite,† it cannot be used for sulphur waters containing chiefly soluble sulphides, or hydrosulphuretted sulphides, and besides these—as is often the case—hyposulphites.

In waters of this description, the sulphur in combination with hydrogen or metal is determined jointly, in the first place, best by means of cadmium solution, which is as sensitive as any other metallic solution (Expt. No. 85), and is not affected by hyposulphite of soda. The precipitated sulphide of cadmium, however, cannot be weighed directly, as it is liable to contain chloride of cadmium (Expt. No. 86), but the sulphur must be determined in it as directed § 148, II., A 1 or 2. A fresh portion of the water is now taken, and first the free sulphuretted hydrogen is expelled from it, and then the sulphuretted hydrogen which is combined with metallic sulphide; the evolved gases being determined by passing them through an ammoniacal solution of nitrate of silver: or finally the sulphur combined with metal as monosulphide is estimated by the difference (unless a bisulphide is present).

For this purpose, the same method may be employed which SIMMLER ‡ used in his excellent analysis of the mineral water of Stachelberg. The free sulphuretted hydrogen gas is first expelled from the water by means of pure hydrogen gas, with the aid of an exhausting syringe; and solution of sulphate of manganese is then added, through a funnel tube, when the sulphuretted hydrogen present as sulpho-acid in combination with metallic sulphide is liberated, and is also removed.

The sulphide of manganese is filtered off, and the warm filtrate mixed with solution of neutral nitrate of silver; if a hyposulphite is present, a precipitate of sulphide of silver is produced, which generally contains chloride of silver also; this is filtered off, the chloride of silver removed by ammonia, the washed sulphide of silver dissolved in nitric acid, the silver in the solution determined as chloride of silver, and the hyposulphurous acid calculated from the result, § 168. Of course the silver in the sulphide need not be determined at the well.

The filtered precipitate of sulphide of manganese contains the sulphur which was present in the water in form of monosulphide; but if the water contains a bisulphide (in which case it will appear yellowish in large bulk) the protosulphide of manganese is mixed with the sulphur which was combined with the monosulphide to bisulphide: this free sulphur is left undissolved on treating the precipitate with hydrochloric acid.

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* SILLIM. Journ. 18, 213; Journ. f. prakt. Chem. 64, 123.

† Compare FRESENIUS'S Analysis of the Mineral Water of Weilbach, Journ. f. prakt. Chem. 70, 8; and of the Gundbrunnen at Frankfort, Jahresber. des physikal. Vereins zu Frankfurt für 1873 bis 1874, 74.

‡ Journ. f. prakt. Chem. 71, 27.

For the details of the operation and the apparatus employed for the expulsion of the sulphuretted hydrogen, the reader is refered to SIMMLER's original memoir.

9. *If the water contains a somewhat large quantity of protocarbonate of iron*—which is indicated by the rather dark violet colour produced on adding gallic or tannic acids—an attempt should be made to determine the protoxide of iron volumetrically with the aid of the dilute solution of permanganate of potassa (§ 207, 16. Comp. Vol. I. p. 218.). About 500 c. c. of the water is used, and the experiment performed in a white bottle, standing on a sheet of white paper; the water must previously be mixed with dilute sulphuric acid.

Several experiments are made until sufficiently constant results are obtained.* If the water smells of sulphuretted hydrogen, or if it contains a notable proportion of organic substances, this method cannot be employed.† In the case of waters rich in chlorides the result will be too high from the cause mentioned, Vol. I. p. 219, unless the precautionary measures there given are adhered to.‡

10. *To determine the whole of the gases which the water holds in solution*, proceed as follows, according to *a* or *b*, as the water is poor or rich in carbonic acid :—

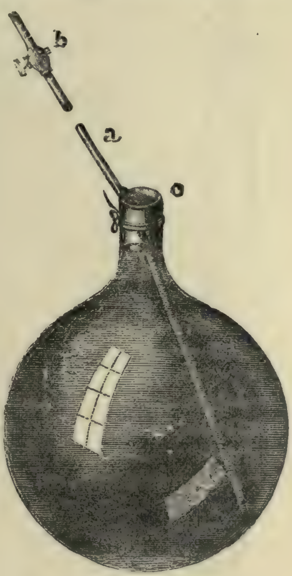

Fig. 81.

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[*] This expeditious process is of great value, as by its help the amount of protoxide of iron which the water of a chalybeate spring loses in its passage to the reservoir, and thence to the baths, may easily be ascertained in a short time; or after being kept for a shorter or longer time in a bottle. The estimations of the iron, which the author made by this process in a preliminary examination of the springs of Schwalbach, corresponded almost exactly with the results of the gravimetric analysis. The same process is also of essential service in prospecting the water of chalybeate springs, as it enables the operator at once to examine on the spot every small contributory with sufficient accuracy.

[†] The following modification, which, however, the author has not yet tried, might be adopted in the analysis of mineral waters in which hydrosulphuric acid only is present with the protoxide of iron :—The relation existing between the solution of iodine and the solution of permanganate of potassa, with respect to their action upon very dilute pure sulphuretted hydrogen water is determined; 500 c. c. of the mineral water is then tested with solution of iodine, and another 500 c. c. with solution of permanganate of potassa: the former process gives the amount of the sulphuretted hydrogen; the latter gives the iron, after deducting from the quantity of permanganate used, an amount corresponding (in its action upon sulphuretted hydrogen) with the quantity of solution of iodine used.

[‡] The peculiar odour, usually perceived while testing acidified saline water with permanganate, frequently arises from bromine or chloride of bromine. During the examination of the Elisabethenquelle, at Homburg v. d. H., the author observed the smell of bromine most distinctly.

a. The water is poor in carbonic acid. A globe, as shown in fig. 81, is filled entirely with the water. For this purpose it is first filled with the mineral water, then let down into the well, either tied to a rod, or with weights attached to it, and the contents sucked out through the gutta-percha tube (*a*), which reaches down to the bottom of the globe, until the water originally present in the vessel is entirely replaced by fresh water from the spring. The cock (*b*) serves to prevent the water in the tube receding during the necessary intervals of cessation from sucking; or a small piece of vulcanized india-rubber tubing may be used for the same purpose closing it by pressing between the fingers. A piece of sheet india-rubber is tied over the mouth of the globe which, by its elasticity, permits the lateral passage of the tube by the side and completely closes the mouth of the globe when the tube is withdrawn. The globe is drawn up out of the well after the suction tube has been removed, and is promptly connected with the flask of a so-called caoutchouc cock,* fig. 82, *a*, which is filled with boiled water, and tied (R. Bunsen).

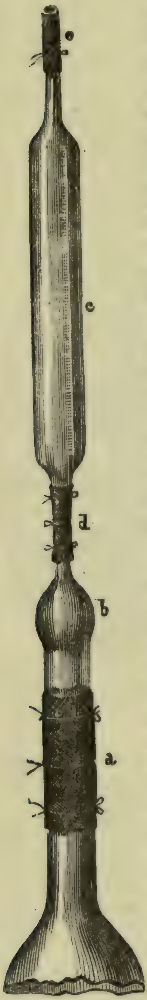

Fig. 82.

If the water flows from a pipe, this is connected with a caoutchouc tube, which is passed down to the bottom of the globe; the water is allowed to run in for some time after the globe is full, and finally closed with the caoutchouc cock as just now directed.

The other end of the cock *a* is then connected with the tube *b*, and the latter again, after pouring some water into it, with the graduated tube *c*, by means of another caoutchouc cock *d*. The capacity of the graduated tube *c* must be at least half as much again as the volume of the gas which the water holds in solution, measured in the cold, and at the common pressure. If this process were used for waters containing much carbonic acid, either the tube *c* would have to be increased to an inconvenient size, or the quantity of water employed would necessarily be so small, that the determination of the other gases dissolved in the water would be impracticable.

The apparatus is now inclined so far as to bring some of the water into the bulb *b*, and this is boiled with the cock *a* closed, and *d* open, until the atmospheric air is completely expelled, and replaced by aqueous vapour; the vulcanized india-rubber tube *e* is then closed by a ligature or a compression cock. When the apparatus is cold, the cock *a* is opened; the water in the globe begins immediately to boil, and the gas which it holds in solution escapes into the vacuum. It is warmed for about 1½ hour, without exceeding a temperature of 90°, which will keep the water in the globe in constant ebullition, and completely expel the gases from it. The flask is then heated a little more strongly, until, owing to the greater expansion of the vapours, the boiled water exactly reaches the ligature *d* of the caoutchouc cock. The instant this is the case, the ligature *d* is tied, the tube *c* removed from *b*, and opened under mercury by untying the ligature at *e*; the volume of the gas, the state of the barometer and thermometer, and the height of the mercury in the tube is then noted (R. BUNSEN*). If there is no graduated tube at hand, a non-graduated one of known capacity can be used instead; in this case, after taking off the ligature, and as soon as the level of the mercury inside and outside is the same, the ligature is again drawn tight, and the mercury which has entered the tube is transferred to a graduated cylinder and measured: the volume found is subtracted from the known capacity of the tube, and the difference is the volume of gas expelled from the water.

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* The contrivance so called has already been described, p. 46.

As it is not convenient to take to the well the entire apparatus required for the actual analysis of the expelled gases, it is better to take the latter to the laboratory in sealed tubes. For this purpose non-graduated tubes similar in form to *c* are substituted for it; these are drawn out at both ends, near the thicker part, so that they can be readily sealed. The gases are expelled from the water, as just described, and, when the boiling out is completed, and the ligature tied round *d*, the tube is sealed at the drawn-out parts in the blowpipe flame, as in fig. 83,† or with an eolipile. It is advisable to fill 2 or 3 tubes in this manner. As the total quantity of gas in a definite amount of the water is known by the first experiment, it is a matter of indifference whether the tubes used for carrying the gas to the laboratory contains the whole of the gas expelled from the water, or whether a small quantity of it is left in the globe.

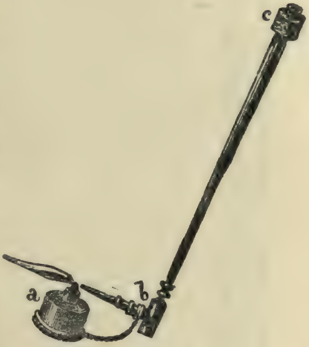

Fig. 83.

Other methods may be used instead of BUNSEN'S. LOTHAR MEYER recommends Ludwig's apparatus, founded on the principle of the barometric vacuum‡ as modified by NAWROCKE.§ He used this apparatus in an analysis of the thermal springs at Landeck.‖

H. McLEOD,¶ heats the water in a vacuum obtained by means of the Sprengel mercury pump.

These methods give good results but require the use of complicated apparatus, full descriptions of which are given in the papers quoted.

b. As already mentioned, the foregoing process is not suitable for waters *rich in carbonic acid*. The escape of the other dissolved gases is then favoured by the abundant evolution of carbonic acid, and the vacuum can therefore be dispensed with. In the examination of such waters, the author proceeds as follows:—A flask holding about 500 c. c.

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* Gasometrische Methoden, 2 Aufl. 18.

† *a* is a small lamp holding about 3 grams oil, connected with the blowpipe by a somewhat flexible wire, so that the flame may be adjusted by bending the wire. The cork *c* serves as the mouthpiece, so that the whole affair may be held and guided with the teeth alone.

‡ SETSCHENOW, Wiener Sitz.-Ber. 36, 293; SCHOFFER, *Ibid*. 41, 9.

§ Zeitschr. f. anal. Chem. 2, 120.

‖ *Ibid*. 2, 236

¶ Journ. Chem. Soc. 22, 307.

is filled with the water, as previously described, and then closed with a perforated caoutchouc stopper that has been well kneaded under the mineral water; into the perforation which is filled with the water, is inserted the end of a tube, entirely filled with the distilled water. This tube is bent first at a right angle, then at an obtuse angle, and is turned up at the end. It is by no means difficult to obtain the flask and the gas delivery tube perfectly full of water. The flask is placed on a wire gauze, and the end of the tube dips into a dish containing boiled potash solution of about 1·27 sp. gr., in which is inverted a tube of the form indicated by fig. 84, also filled with potash solution; the part *a* holds about 5 c. c. Before use, a strip of paper is gummed on *b*, which is marked as shown—the numbers indicating the capacity of the portion of the tube above them in c. c. The graduation may be performed with ease and rapidity as follows:—hold the tube under a Mohr's burette, and run in water until it has passed the shoulder; continue adding water, till a whole number of c. c. has been run in, and then make the first mark, add another c. c. and mark again, &c. As soon as the mouth of the gas delivery tube has been brought under the opening of the inverted tube, begin to heat the flask slowly. The escaping carbonic acid is absorbed by the potash, the unabsorbed gases collect in *a*. The water is gradually heated to boiling and the boiling continued until the volume of gas ceases to increase, the delivery tube is then removed, and the whole allowed to cool. The volume of gas indicated by the scale is noted, also the pressure and temperature, and the part *a* of the tube is then fused off by means of an eolipile or the apparatus fig. 83: the gas can then be removed to the laboratory and examined at leisure. Should the gas from one operation not reach the scale, that from a second quantity of the water must be passed into the same tube. It is advisable also to fill another tube in the same manner. There are two sources of error involved in this method: first, the exact volume of the water from which the gas is produced is not known—this arises from the fact that, on warming the water, a portion is driven into the tube, before its gas has been expelled, and although afterwards strongly heated, one cannot be certain that it loses every particle of gas—secondly, the tension of the water contained in the potash solution cannot be exactly calculated. The error is, however, decidedly smaller than if a small quantity of highly aërated water is treated after the method *a*, when the amount of unabsorbed gas is scarcely measurable.

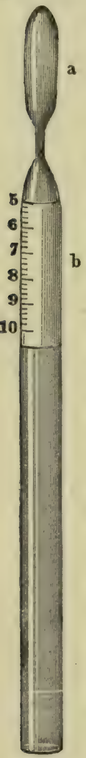

Fig. 84.

11. If it is wished to ascertain accurately the nature of the gases *spontaneously disengaged* from the spring, they should be received in test-tubes holding 40 to 60 c. c., connected air-tight with a funnel by means of a cork or caoutchouc tube, as shown in fig. 85. These tubes are drawn out at *a*, to the thickness of a thin straw. If larger quantities of gas are required it is collected in bottles with drawn-out neck (fig. 86.) After the tubes or bottles have been filled with the mineral water, and connected air-tight with the funnel, the apparatus, with the mouth of the funnel turned upward, is completely submerged, and water sucked out through a narrow tube, reaching down to the

bottom of the tube or bottle, until the water of the first filling is entirely replaced by a fresh quantity, which has not been in contact with air. The apparatus is now inverted, under the water, and the spontaneously disengaged gas ascends through the funnel. Should the gas-bubbles be detained in the neck of the funnel, or below the narrow part of the tube or bottle, they may readily be dislodged by tapping the rim of the funnel against a hard body.

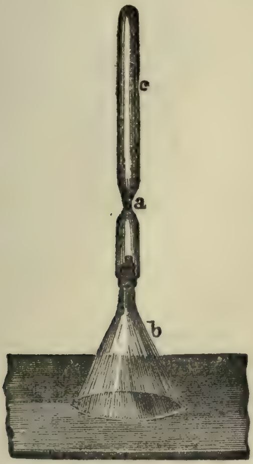

Fig. 85.

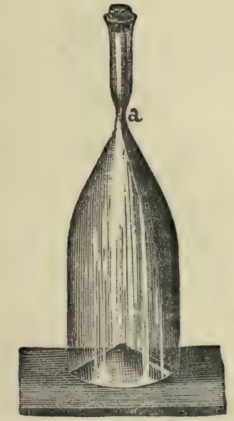

Fig. 86.

As much gas is allowed to enter as will fill the tube or bottle and the neck of the funnel, a dish is then placed beneath the funnel, and the apparatus lifted out of the water; the narrowed part of the tube or bottle is gently heated to remove moisture, and then sealed. As the column of water in the funnel above the level of that in the dish diminishes the pressure of the gas against that of the atmosphere, there is no fear that the glass will blow out in sealing (R. Bunsen*). For warming and fusing off the tube an eolipile or blow-pipe and lamp (fig. 83) is used. It is necessary to fill several tubes or bottles in this manner.

Should the nature of the spring be such that it is impossible to fill the tubes in the manner described, recourse is had to the following contrivance (R. Bunsen).† The funnel is weighted by the lead ring *c*, and lowered into the well with a strong cord. The tube of the funnel is connected by india-rubber with the tin tube *ab*, and the latter with three or four glass tubes, *c*, *c*, *c*, each of a capacity of 40–60 c. c., and at the parts where they are to be fused off somewhat thickened and narrowed. The funnel is first filled by suction as far as the cock *b*, and the gas is then allowed to ascend in the funnel till it is under a pressure exceeding that of the atmosphere. The cock *b* is then opened and the gas is allowed to pass through *c*, *c*, *c*, until it is certain that all atmospheric air has been dislodged. The tubes *c*, *c*, *c*, which are connected with one another by short pieces of small caoutchouc tube being now filled with gas from the spring, are warmed, and then the two outside caoutchouc connectors are closed air-tight by compression with the fingers or by a clamp ; finally, as soon as the temperature has fallen so that the outside atmospheric pressure is slightly superior to the inside pressure, the tubes are fused off in succession.

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* Gasometrische Methoden, 2 Aufl. p. 3.

† *Ibid.* p. 5.

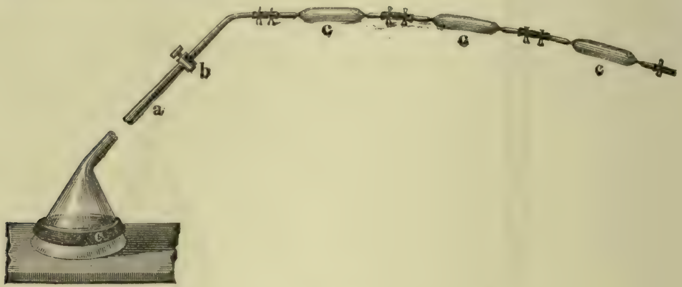

Fig. 87.

Very often in the case of chalybeate springs, carbonic acid predominates so largely in the spontaneously disengaged gas, that a large number of tubes must be filled, so that after the absorption of the carbonic acid by potash, there may be a sufficient quantity of the other gases (nitrogen, marsh gas, oxygen) for examination. In such cases the author prefers to determine the proportion between the volumes of the gases absorbable and not absorbable by potash, and to collect for transport to the laboratory none but the unabsorbable gases.

To effect the first, a graduated cylinder 20 to 30 mm. wide, and holding 200 to 300 c. c. is filled with the mineral water by sucking out what first enters with a glass tube, and is then inverted either in the basin of the spring itself, or in a porcelain dish filled with the mineral water according to circumstances. It must be filled *entirely* with the gas, in the first case directly, in the second by the aid of the weighted funnel above described, which must now be provided with flexible tube and gas evolution tube instead of collecting tubes. The cylinder is removed from the well with a porcelain dish, the confining water sucked out of the dish almost entirely with a pipette, replacing it by boiled potash solution, and the cylinder is then agitated to favour the absorption of the carbonic acid. When this is finished, the volume of the unabsorbed gas is read off, noting the temperature and pressure. In many cases, even when large cylinders are used, it would be impossible to measure the unabsorbed gas, unless the upper portion were narrowed as in fig. 88.

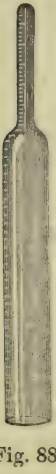

Fig. 88.

In order to collect the unabsorbable gases alone, the author always uses the weighted funnel, with narrow gas tube and flexible connector, provided with a screw pinchcock. The gas tube dips into a dish containing boiled potash solution, in which a tube of the form fig. 89 is inverted. The clip being open, as soon as it is quite certain that the gas coming from the funnel is entirely free from atmospheric air, the turned-up end of the gas delivery tube is placed under the tube fig. 89, and the gas allowed to rise in a regular succession of small bubbles by adjusting the screw clip. As these will be almost completely absorbed, it will of course be some time before the tube is filled to about *a*, and ready for sealing off.

12. If sulphuretted hydrogen is given off, a rather large-sized flask with the neck somewhat drawn out, is filled with the mineral water, a piece of wide caoutchouc tubing purified with soda and provided with a strong compression cock is pushed over the neck, a funnel is inserted into the other end of the caoutchouc tube filled with water, and the whole inverted under the surface of the water, to receive the gases. When the flask is full, the compression cock is closed, and the flask inverted in a beaker containing solution of chloride of copper mixed with ammonia in excess; the compression cock is then opened, and a sufficient quantity of the solution allowed to enter the flask; after which the cock is closed, the flask shaken, and the mixture allowed to remain at rest for some time. The sulphide of copper formed is then collected, and the sulphur in it determined as directed § 148, II. A. 2, *a*, the volume of the sulphuretted hydrogen being calculated from the quantity of sulphur; the volume of the carbonic acid is obtained by subtracting this from the gases absorbed by solution of potassa (determined in 11).

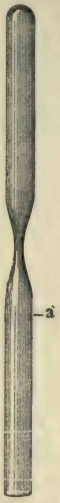

Fig. 89.

13. To determine the specific gravity of highly aërated mineral waters, the bottles shown in fig. 90 may be used with advantage. They hold 200 to 400 c. c. The thin part of the neck is 50 mm. long, cylindrical, and as uniform as possible in the bore, its internal diameter but 5–6 mm.; it is provided with an etched millimetre scale. The mouth of the bottle must be quite round, so that it may be closed airtight with a caoutchouc stopper. To fill a bottle of this kind, it should be plunged under the surface of the water, inserting a narrow tube to allow the air to escape readily: in this way it can be filled without difficulty. The glass tube must be gradually raised as the water enters and is at last taken away. As soon as the water level reaches halfway up the drawn-out neck, the mouth is closed under water with the thumb, the bottle at once taken out, and the caoutchouc stopper firmly inserted and tied down. It is as well to fill three or four bottles in this way. Each must be carefully packed in a separate cardboard box, so that they may not be broken during carriage. In default of these bottles, several ordinary medicine bottles with ungraduated necks should be filled with the water in the manner described.

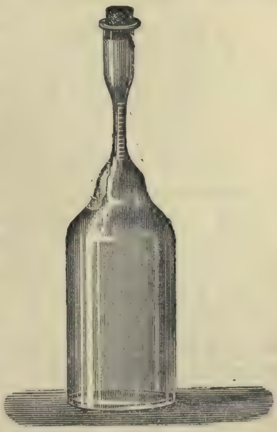

Fig. 90.

14. Attention should be paid to every particular connected with the spring, and in fact, to every circumstance which may have a bearing on the investigation: as, for instance, how much water and how much free gas the spring yields; whether these quantities remain the same

at different periods of the year, and with the changes in the height of the water in neighbouring rivers; whether the level is constant; whether a muddy deposit or solid sinter is formed in the outlet pipes or in the reservoir (in which case a tolerably large quantity of it should be taken to the laboratory for examination); to what geological formation the mountain belongs on which the spring comes to the surface; the depth from which the spring rises; the nature of the basin; the predominant action of the water, &c.

B. Operations in the Laboratory.

I. Qualitative Analysis.

This is effected in the manner described in the "Qualitative Analysis," § 211, *et seq.**

II. Quantitative Analysis.

§ 209.

The course to be pursued in the quantitative analysis of mineral waters differs according to the presence or absence of alkaline carbonates. As the analytical course is more simple in the case of *alkaline waters*, (as those which contain alkaline bicarbonates are called) the methods employed for these will be considered first, starting on the supposition that all the substances usually found in alkaline waters are present. The modifications required for the examination of saline waters and of sulphuretted waters will be described subsequently.

Determination of the Specific Gravity.

a. The water is poor in gas.

A bottle of the mineral water and a bottle of distilled water are brought to the same temperature, and the height of the thermometer noted. An accurately tared small bottle of at least 100 grams capacity, provided with a well-fitting glass stopper, is filled with the distilled water and weighed, then filled with the mineral water, and weighed again. The quotient obtained by dividing the weight of the mineral water by that of the distilled water, gives the sp. gr. of the former. It is better, however, to use a pyknometer, fig. 91, consisting of a flask with a long perforated ground stopper. Great care should be taken that there are no gas bubbles adhering to the sides of the bottle, and also that it is not made warm by contact with the hands when it is being dried. The use of a pyknometer with thermometer ground in offers the best security against any inequality of temperature in the liquids to be weighed.

b. The water is highly aërated.

Here the method *a* is inapplicable unless the water be first deprived of a portion of its carbonic acid. If this be done, however, it is evident that the result will not be the true sp. gr. of the water as yielded by the spring, and will, moreover, vary with different analysts. The determination of the sp. gr. of such water may be made with the aid of the bottles described in § 208, 13, and filled as directed.

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* Mineral waters which have been kept a long time in stone bottles, often have an odour of sulphuretted hydrogen, although they were quite free from it in the fresh state. This is owing to the moist cork, or some other organic substance, reducing a portion of the sulphates to sulphides, from which the free carbonic acid afterwards evolves sulphuretted hydrogen.

The bottle is placed in a room of tolerably constant temperature on a horizontal support, and by its side a somewhat larger bottle containing distilled water, closed with a cork, through which a thermometer passes and dips into the water. After a lapse of twelve hours the contents of both bottles will certainly be of the same temperature. The thermometer is now read off, and also the height of the mineral water on the scale which is best done by means of a telescope, in a horizontal position, movable up and down on a vertical rod, and six or eight feet distant.

The bottle with its caoutchouc stopper is weighed on a sufficiently delicate balance, the cork is taken out without wetting it, the bottle emptied, rinsed and filled with distilled water to slightly above the mark at which the mineral water stood; the bottle is then completely dried, left for a sufficient time near the other bottle containing the thermometer, and the water removed from the neck until the height is the same as it was when it contained the mineral water. Finally, after carefully observing that the temperature has not altered, the caoutchouc stopper is inserted and the bottle weighed. The weight of the empty dry bottle and cork—which must be ascertained now if not previously determined—is deducted from both of the two weights obtained, which gives the necessary data for the accurate calculation of the sp. gr. of the water.

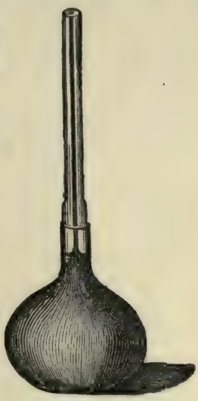

Fig. 91.

In default of bottles of the above description, the sp. gr. may be determined by means of common narrow-necked medicine bottles; in this case, fine points made on three narrow strips of paper, gummed on the neck, supply the place of the engraved scale.

The several quantities required for the following estimations may be determined directly by weight or by measure, multiplying the number of c. c. by the sp. gr. of the water to find the weight.

The author prefers to weigh the quantities, as they are then quite independent of the temperature, moreover, when it is advisable the entire contents of a bottle can be used, or quantities of the water can be taken weighing a round number of grams.

1. Estimation of the Total Amount of the Fixed Ingredients.

For this purpose the contents of a large or small bottle, some 200 to 2000 grams, according to the concentration of the mineral water, are carefully evaporated in a weighed platinum dish at a temperature below the boiling point, filling up the dish from time to time. If the water contains much gas, the dish must be covered with a clock-glass at the commencement and after each fresh addition of water. It is safest to evaporate on the water-bath, but with care it may be done over a lamp with a small flame: it must, however, be completed on the water-bath and the residue dried in an air-bath or oil-bath at 180°, until the weight is constant: this is noted. The dish is now half filled with distilled water, and hydrochloric acid added drop by drop until all the carbonates are decomposed, taking care to keep the dish covered with a clock-glass as much as possible during the operation; it is then warmed gently to drive off the liberated carbonic acid, the cover washed into the platinum dish, and pure dilute sulphuric acid added in quantity sufficient to convert all the bases into sulphates, avoiding any great excess. Finally, the contents of the dish are evaporated to dryness, and gently ignited for some time with repeated addition of small quantities of solid carbonate of ammonia, until the alkaline acid sulphates are converted into neutral sulphates and the weight becomes constant.

If any residue remains in the bottle which cannot be washed out, it is dissolved off with nitric acid, the solution evaporated to dryness, the residue ignited and treated as above described; the weight must be added to that of the principal residue.

In determining the fixed residue of waters rich in iron, it is best to choose a bottle in which, from long exposure to the air, the whole of the iron has been deposited as hydrated oxide of iron. The sample is filtered, the precipitate washed, and the filtrate treated as described. The precipitate is treated with nitric acid, which leaves a residue of silica; this is to be determined and the weight added. The nitric acid solution is evaporated, the residue ignited, treated with water and carbonate of ammonia to convert some caustic lime into carbonate, and heated moderately so as not to decompose the carbonate of lime again; it is then weighed, and the weight added to that of the contents of the platinum dish dried at 180°.

The iron oxide is then treated with hydrochloric acid and sulphuric acid, evaporated and ignited; the weight thus obtained has to be added to the weight of the sulphates from the water.

By proceeding in this way, the difficulty is avoided, which arises in the ordinary method, where the sulphate of magnesia is liable to be decomposed, if the residue is too strongly heated, whilst if it is insufficiently heated some sulphuric acid remains in combination with the oxide of iron.

Hereafter the use of the solid residue and the sulphates &c. in controlling the analysis will be fully explained.

2. Estimation of the Chlorine, Bromine and Iodine.

For this purpose from 200 to 2000 grams of the water is employed according to the amount of chlorine it contains. If the quantity of chlorine in the water is relatively large, it is at once acidified with nitric acid precipitated with silver nitrate and the precipitate determined according to § 141, 1, *a*, as chloride of silver containing some bromide and iodide of silver, or it may be converted into metallic silver by ignition in a current of hydrogen (§ 115, 4, *a*). Water containing only a small proportion of chlorine should be evaporated down to about one-fourth before adding the nitric acid. It is then filtered, washed, and the filtrate treated as above.

3. Estimation of the Silicic Acid, Iron, Manganese, Alumina, Lime (together with Baryta and Strontia) and Magnesia.

Some 2000 to 7000 grams of the water is used for this purpose, being the contents of one or more bottles. The determinations, especially of the iron, can only be correct when the water is clear and free from ochreous flocks (compare § 208, 6). After weighing the bottle or bottles, the neck is smeared with the smallest possible quantity of grease, and a portion of the contents poured out carefully into a beaker so as not to lose a drop; hydrochloric acid is now added in slight excess both to the water in the beaker, and also to the bulk remaining in the bottle. The whole of the acidified water is now evaporated carefully to dryness in one or more large platinum dishes finishing on the water-bath* (§ 140, II. *a*), the residue moistened with hydrochloric acid, water added after some time, the whole warmed, and the insoluble silicic acid collected, washed thoroughly, and weighed. After the weighing, it is heated with sulphuric acid and pure fluoride of ammonium or hydrofluoric acid; if there is any non-volatile residue (small quantities of sulphate of baryta, or titanic acid†) it must be taken into account.

The liquid filtered from the silicic acid is then precipitated with ammonia (best in a large platinum dish), and the precipitate after being warmed is collected and washed. This precipitate, consisting for the most part of oxide of iron, is again dissolved in hydrochloric acid, neutralized with a dilute solution of carbonate of ammonia almost until it becomes turbid, then boiled, and the precipitate, which is now quite free from manganese and the alkaline earths, collected. If ammonia produces traces of precipitate in the filtrate, it is collected, dissolved in hydrochloric acid, again precipitated with ammonia, collected and added to the precipitate first obtained.

The large precipitate of basic iron salt and that subsequently obtained by ammonia are again dissolved in hydrochloric acid, pure acid tartrate of potassa added (the acid tartrate often contains alumina) then ammonia, and the iron precipitated from the clear solution by means of sulphide of ammonium in a flask which must be nearly filled and closed; in this way it is separated from alumina and phosphoric acid. The sulphide of iron is dissolved in hydrochloric acid, oxidized with nitric acid, precipitated with ammonia, collected, ignited, and weighed as *sesquioxide of iron*. After it has been weighed, it is dissolved in fuming hydrochloric acid to see if there is any residue other than that due to the filter ash. If there is, it (silicic acid) must be deducted from the weight of the oxide of iron.

The liquid filtered from the sulphide of iron is evaporated to dryness in a platinum dish with some carbonate of soda solution which is perfectly free from alumina (prepared by saturating with carbonic acid, allowing to stand for a long time, and filtering); the residue is then heated with some pure nitrate of potassa, washed out into a beaker with water, dissolved in hydrochloric acid filtered and precipitated with ammonia; generally a few flocks of phosphate of *alumina* are obtained. If this is the case, as it usually is, molybdate of ammonia gives a precipitate with the phosphoric acid in the filtrate; if it does not, the phosphoric acid must be determined in the weighed alumina precipitate.

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* If porcelain basins are used the estimation of the silicic acid is interfered with, whilst that of the alumina is valueless.

† In order to test a residue of this kind, it should be fused with acid sulphate of potassa, and this treated with cold water and filtered; titanic acid goes into solution, and separates again on long-continued boiling, whilst the sulphate of baryta remains undissolved.

The filtrate containing the manganese, lime and magnesia is slightly acidified with hydrochloric acid, concentrated, and the manganese precipitated by sulphide of ammonium. The flask, which should be very nearly full, is allowed to remain at rest for twenty-four hours in a moderately warm place, the precipitate is then collected, washed, dissolved in hydrochloric acid and again precipitated with sulphide of ammonium. Finally, the sulphide of manganese, mixed with sulphur, is ignited in a current of hydrogen and weighed; its purity must be tested as described in § 109, 2.

The filtrate is heated with hydrochloric acid, evaporated, filtered from the sulphur, and the lime precipitated with oxalate of ammonia and ammonia. When the precipitate has subsided, it is collected, washed, ignited, dissolved in hydrochloric acid, again precipitated with ammonia and oxalate of ammonia, collected, and the oxalate of lime, weighed as carbonate or sulphate, or as caustic lime (§ 103, 2*b* and § 154, 6). As a rule it contains strontia which, when it has been determined (as in 6), must be deducted, to find the true weight of the lime present.

The united filtrates are evaporated to dryness, ignited in a platinum dish to remove ammonium salts, moistened with hydrochloric acid, evaporated on the water-bath to dryness, taken up with hydrochloric acid and water, and the magnesia precipitated with phosphate of soda and ammonia and weighed as hydrophosphate (§ 104, 2). The absence of lime should first be ascertained by testing some of the solution with ammonia and oxalate of ammonia.

If the mineral water is so rich in lime and magnesia that 2000–7000 grams of it would give too large a precipitate, the filtrate from the manganese after heating, evaporating, acidifying, and filtering is made up to one litre, and an aliquot part (a half or a quarter) of it taken for the estimation of the lime and magnesia.

4. Estimation of the Sulphuric Acid, Soda and Potassa.

The contents of one or two bottles, from 2000 to 6000 grams of the water, is acidified with hydrochloric acid, evaporated, and the silica separated as in 3. The filtrate, which should be free from any great excess of hydrochloric acid, is then carefully precipitated hot with chloride of barium. The precipitated sulphate of baryta is first weighed as it is, then warmed with hydrochloric acid and washed; the acid washings are evaporated almost to dryness with a few drops of chloride of barium solution, water is added, and the small quantity of sulphate of baryta collected; this is added to the original precipitate and the two weighed together (§ 132, 1). From this the correct amount of sulphuric acid can be calculated. If there is any weighable quantity of sulphate of baryta with the silica, this must be added to that previously found.

The filtrate from the sulphate of baryta is evaporated to dryness on the water-bath, the residue extracted with water, and the solution boiled with a slight excess of pure milk of lime (§ 153, 4, *a*, *β*) filtered and precipitated with ammonia and carbonate of ammonia, and finally a little oxalate of ammonia. The filtrate from the precipitate thus produced is evaporated to dryness, ignited in a platinum dish to drive off ammonia salts, and treated again in the same way to remove the last traces of magnesia, using however carefully measured quantities of the re-agents. After the final ignition in a covered platinum dish, the residue, consisting of chlorides of the alkali metals, is weighed.

In order to separate the chloride of potassium from the chloride of sodium and the small quantity of chloride of lithium, they are all converted into platinochlorides by adding excess of perchloride of platinum, treating with alcohol of 80 vol. per cent., filtering, washing with alcohol (§ 152, 1, *a*), and drying on the filter. When the platinochloride of potassium has been transferred to a small weighed platinum dish, the remainder is dissolved off the filter with boiling water, the whole evaporated to dryness, dried at 130°, and weighed as platinochloride of potassium. In order to ascertain if this is pure, it is treated repeatedly with small quantities of cold water; some bichloride of platinum is then added to the solution, which is evaporated almost to dryness, treated with alcohol, and filtered; the small quantity of platinochloride of potassium left on the filter is dissolved off with boiling water, and evaporated in the platinum dish with the principal quantity, and weighed after being dried at 130°. If the weight is not the same as that originally obtained, it shows that the original precipitate of platinochlorides contained some sodium or lithium. The last weighing is taken as the correct one, and the amount of potassium calculated from it. The amount of chloride of sodium and consequently that of the sodium is ascertained by subtracting the weight of the chloride of potassium from the total weights of the chlorides of the alkali metals, after that of the chloride of lithium has been deducted (the method of estimating this will be given hereafter).

In order to be quite certain that the alkaline chlorides contain no trace of the alkaline earths, the solution of the mixed sodium and lithium platinochlorides is evaporated to dryness, heated in a current of hydrogen, and treated with hydrochloric acid and water; the solution, after being filtered from the metallic platinum, is tested for baryta by means of sulphuric acid, for lime by ammonia and oxalate of ammonia, and for magnesia by phosphate of ammonia and soda. If traces of the alkaline earths are found, they must be estimated and the corresponding weights of their chlorides deducted from the sum of the chlorides of the alkali metals.

The amount of the alkalies combined with carbonic acid is determined indirectly with sufficient accuracy by calculation from the results of the analysis, provided always that this has been made carefully. Of methods for their direct estimation, which may be used with advantage in a preliminary examination of alkaline mineral waters, the following is recommended:—600 to 800 grams of the water are boiled for a long time, filtered, and the precipitate washed with hot water. The filtrate, together with the washings, is divided into two equal parts, one of which is concentrated, and the alkaline carbonate therein determined volumetrically, § 220 (together with the traces of lime and magnesia present), whilst the other is used to determine the lime and magnesia. In this way a correction can be applied to the first result as the carbonates of lime and magnesia act on acids in the same way as the equivalent quantity of carbonate of soda.

5. Estimation of the Total Carbonic Acid.

The flasks previously prepared at the spring (§ 208, 7), serve for this purpose. These are first weighed, and then—if only a short time has intervened between the filling and the analysis—heated for some time in a water-bath (*b*, *a*, Vol. I. p. 331). The bulk of the clear liquid is filtered through a small plaited filter,* without disturbing the precipitate, and the filter, without washing, is introduced into the flask containing the precipitate and the rest of the fluid; the carbonic acid is then determined according to § 139, II., *e* (p. 340). In mineral water containing much carbonic acid, especially if many estimations have to be made, the carbonic acid may be collected in a weighed Geissler's potash bulbs (fig. 45, p. 34), and a soda-lime tube placed behind them. The potash bulbs are refilled for every alternate operation, and the frequent filling of the soda-lime tube is thus avoided. The results leave nothing to be desired (Expt. No. 87). If the original mineral water has been measured, the number of c. c. taken must be multiplied by the sp. gr. to obtain the weight of water corresponding with the carbonic acid found.

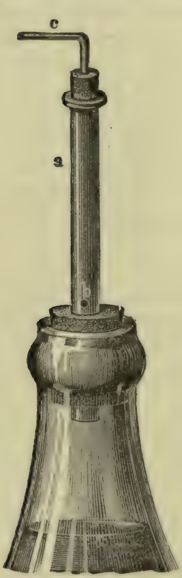

Fig. 92.

In determining the carbonic acid in mineral waters contained in bottles, a loss of the gas would be unavoidable on removing the cork, if the water were supersaturated with carbonic acid. In such cases it is necessary in the first place to estimate the carbonic acid, which escapes when the pressure of the cork is removed, and then that which remains in solution in the water. Numerous devices have been proposed for boring the corks without loss of gas; the simplest is that of FR. ROCHLEDER,† illustrated in fig. 92, *a* is a cork-borer provided below with a lateral opening *b*, and above with a perforated cork, and tube *c* fitting air-tight. The borer being inserted as represented—by this operation, no air either enters or escapes—*c* is connected with the apparatus for drying and collecting carbonic acid described Vol. I. p. 340, *e*, by means of a flexible tube, provided with a screw clip, and the borer turned slowly downwards. As soon as *b* is passed quite through the cork, the carbonic acid begins to issue from the bottle, the stream being regulated by the clip. When the evolution of gas ceases, the bottle is removed and air freed from carbonic acid is drawn through the system of tubes. The increase of weight in the absorption apparatus together with the amount of carbonic acid in the upper part of the bottle gives the carbonic acid lost by the water on the removal of the pressure. Immediately after the bottle has been disconnected from the apparatus, water is drawn out of it with a syphon, and the carbonic acid determined in the water in the manner described, § 139, 1 *b*, *a*, Vol. I. p. 331.

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* The filtrate must have a strongly alkaline reaction, and remain clear on adding chloride of calcium.

† Zeitschr. f. analyt. Chem. 1. 20.

6. Estimation of the Iodine, Bromine, Lithium, Baryta, and Strontia.*

The contents of a carboy (about 60 litres) is evaporated down to about 4 or 5 litres in a tinned copper or iron pot, the alkaline solution filtered, and the residue washed with boiling water until the washings are no longer alkaline. The residue should be tested spectroscopically to see that it no longer gives the lithium lines.

The solution *A* serves for the estimation of the iodine, bromine and lithia, the residue *B* for the alumina, manganese, baryta, and strontia.

A. The Aqueous Solution.—This is evaporated until a moist saline mass is left, which is then rubbed up with a considerable quantity of alcohol of 96 per cent., using a pestle; the solution is filtered, and the residue boiled three times successively with alcohol. After a drop or two of strong potash solution has been added to the alcoholic filtrate, the alcohol is distilled off; the residue thus obtained is then dissolved in water, again evaporated, and the saline mass treated with alcohol in precisely the same manner as the original residue. The alcohol is distilled off from the solution thus obtained, and the residue again treated in the same way By this means a solution is obtained containing all the alkali-metal iodides and bromides with a comparatively moderate quantity of the chlorides. After two drops of potash solution have been added to it, it is evaporated to dryness in a platinum dish, heated to low redness,† and completely extracted with boiling water. If the solution has a brown colour, it is again evaporated to dryness with two drops of potash solution and a very small quantity of nitrate of potassa, and the residue is again gently ignited. On again extracting the residue with water, a clear colourless solution is obtained. This is mixed with bisulphide of carbon acidified with dilute sulphuric acid, and a small quantity of a solution of nitrous acid in sulphuric acid is added; the whole is then shaken, when the bisulphide of carbon takes up the iodine and becomes violet coloured. It is separated from the aqueous solution, washed, and the iodine in it determined by a very dilute solution of hyposulphite of soda of known strength (§ 145, 1 *b* β). The chlorine and bromine in the solution is separated from the bisulphide of carbon and precipitated by silver nitrate, and the bromine in it estimated by heating a weighed portion of it in a stream of chlorine (§ 169, 1 *a*).

The excess of silver in the filtrate from the chloride and bromide of silver is precipitated by hydrochloric acid and the filtrate reserved.

To determine the lithia (and some other substances present in small quantity in the solution *A*), the saline residues insoluble in alcohol are used, together with the two filters (these must be incinerated) through which the solutions containing iodides, bromides, and chlorides of the alkali metals were filtered, and the solution from which the excess of silver has been precipitated by means of hydrochloric acid. These three are mixed, water added, then hydrochloric acid in excess, and the solution filtered if necessary, poured into a 1 or 2 litre flask, made up to the mark and shaken (the silica filtered off may contain titanic acid).

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* If the amount of manganese or alumina is so small that they cannot be determined in the water used for 3, they must be estimated in this larger quantity, as also the other acids and bases (cæsia, rubidia, the oxides of zinc, nickel, cobalt, copper, lead, thallium, and antimony, boric acid, arsenious acid, arsenic acid, and titanic acid). if any of them are present in quantity sufficient to render a determination possible.

† If the residue is very strongly heated, there may be a considerable loss of iodine owing to the decomposing action of the chlorides on potassium iodide (Ubaldini, Compt. rend. 49, 306; Jour. f. prakt. Chem. 84, 191), whilst by heating to low redness in presence of hydrate of potassa there is no loss of iodine. Compare Fresenius, Zeitschr. f. anal. Chem. 5, 318.

To determine the lithia, an aliquot part of this solution is used, usually a fourth is enough, corresponding with 15 litres of the original water (some idea may be obtained of the quantity necessary to be employed by evaporating some of the original water and examining it spectroscopically). This portion also serves for testing for cæsium, rubidium, and thallium. The remainder may be used for the detection or estimation of boric acid, and also for testing for arsenic.

a. The measured portion of the solution for the lithia is evaporated almost to dryness, the residue triturated with absolute alcohol in sufficient quantity, filtered, and the residue boiled out with successive small quantities of strong alcohol until neither the residue of chloride of sodium nor the alcoholic extract gives the lithium spectrum. The alcoholic solution is then distilled down, the residue dissolved in water acidified with two drops of hydrochloric acid, and evaporated until a moist saline mass is left; this is then treated in precisely the same manner as the original residue, the series of operations being repeated several times. The last time, the alcohol is mixed with half its volume of ether. In every instance the residue must be examined spectroscopically to see that it is free from lithium.

The ether-alcohol solution is distilled down, the residue moistened with water, a little hydrochloric acid added, and the liquid evaporated to dryness at 100°. It is then dissolved in water, two drops of ferric chloride solution and a little pure milk of lime added to precipitate any phosphoric acid present, and the solution filtered from the precipitate (consisting chiefly of hydrate of magnesia), which is washed with water until it no longer gives the lithia reaction. The filtrate is precipitated with oxalate of ammonia, the precipitate washed, ignited, dissolved in hydrochloric acid, evaporated and tested for lithium; if it contains any, the solution must be again precipitated with ammonia and oxalate of ammonia.

The filtrate (or both filtrates) from the oxalate of lime is evaporated to dryness, the ammonia salts driven off, the residue moistened with hydrochloric acid, and water added; the solution is then evaporated to dryness at 100°, and the treatment with milk of lime, &c., repeated, using small, carefully regulated quantities of re-agents. The precipitates must always be examined for lithium. After repeatedly driving off the ammonia salts, moistening with hydrochloric acid, and evaporating at 100°, the lithium is separated as phosphate of lithia (§ 100), weighed, and examined to see if it dissolves in hydrochloric acid without residue, or whether the somewhat diluted solution gives a slight precipitate in the cold when supersaturated with ammonia. If this is the case, it must be again dissolved in hydrochloric acid, precipitated with ammonia, the precipitate collected, weighed, and, together with the small residue insoluble in hydrochloric acid, subtracted from the weight of the phosphate of lithia. Of course these precipitates must be examined to see that they are free from lithia.

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The filtrate from the phosphate of lithia may be utilized for testing for cæsium, rubidium, and thallium, and even for their estimation when the residue from a larger quantity of water is not available. For this purpose the solution is heated to expel the ammonia, then ferric chloride is added, and the liquid carefully neutralized with ammonia so as to remove the phosphoric acid. The precipitate, which should be yellowish-brown and not white, is filtered off, and the filtrate evaporated to dryness and gently ignited to expel ammonia salts; the residue is then dissolved in a little hot water precipitated with concentrated chloride of platinum solution, and the precipitate freed from the greater part of the platinochloride of potassium by repeatedly boiling it with small quantities of water. The residue is reduced in a current of hydrogen at a low red heat, extracted with alcohol, and the residue left on evaporation of the alcoholic solution is tested spectroscopically for cæsium and rubidium, and the insoluble residue for thallium.*

In 60 litres of a mineral water there will scarcely ever be sufficient of these metals to separate them and determine them quantitatively. If, however, this should happen to be the case, the chlorides of potassium, rubidium, and cæsium obtained by decomposing the precipitate obtained by means of chloride of platinum may be separated by adding chloride of tin to the hot concentrated solution mixed with a considerable quantity of hydrochloric acid. In this way the cæsium is precipitated as the crystalline cæsium tin chloride (STOBBA†), whilst the potassium and rubidium remain in solution. The tin is precipitated from the solution by sulphuretted hydrogen, and the chlorine contained in a weighed portion of the mixed chlorides of potassium and rubidium is determined; from this the metals may be estimated in the indirect way (§ 200).

b. The remainder of the solution, in an aliquot part of which the lithia has been determined, may then be used for testing for arsenic and determination of the boric acid.

The solution at 70° is treated with sulphuretted hydrogen, and any precipitate produced is tested for arsenic (also for antimony). The filtrate is freed from sulphuretted hydrogen by continued warming at a gentle heat (it must not be boiled), carbonate of potassa in slight excess is added, and the whole evaporated to dryness; the residue is then extracted with alcohol and a little hydrochloric acid (the insoluble residue may contain titanic acid), potash solution is added to the filtrate to strongly alkaline reaction, the alcohol distilled off, and the residue boiled with water and some carbonate of potassa to precipitate the last traces of lime. The filtrate is acidified with hydrochloric acid, and the phosphoric and boric acids separated (§ 166, 3 *c.*), and the latter estimated, § 136, I. 1 *d.* (Vol. I. p. 321).

B. The Residue Insoluble in Water.—This is mixed with water in a large porcelain basin, hydrochloric acid in excess is added, and also

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* R. BÖTTGER, using this process, found thallium in the saline residue from the Nauheim mother liquors. If the extract of this saline mass made with 80 per cent. alcohol is precipitated with an insufficient quantity of chloride of platinum, a platinochloride of potassium containing cæsium and rubidium is obtained, whilst the aqueous extract of the residue precipitated in a similar way yields platinochloride of potassium containing thallium. (Beglückwünschungsschrift des Frankf. physik. Vereins zur Jubelfeier des hundertjährigen Bestehens der Senkenberg'schen Stiftung, 1863.)

† Zeitschr. f. anal. Chem. 12, 440.

5 drops of dilute sulphuric acid. If any of the residue remains adhering to the pan it is removed by means of dilute acetic acid, the solution added to the main bulk of the liquid, and the whole evaporated to dryness. The residue is treated with hydrochloric acid and water and filtered from the silica, &c. The precipitate is boiled with a solution of carbonate of soda until the silica appears to be dissolved, the solution filtered, using a hot-water funnel, and the residue washed (the silica may be precipitated from the solution and tested for titanic acid). The filter containing the residue is incinerated, fused with carbonate of soda, and the product boiled with water and filtered from the small residue of carbonate of baryta, &c. (The silica may be precipitated from the solution and tested for titanic acid.) The precipitate is washed, dissolved in dilute hydrochloric acid, and any lead present is removed by treatment with sulphuretted hydrogen; the filtrate from the lead sulphide is then evaporated on the water bath, the residue taken up with water and a few drops of hydrochloric acid, and precipitated with a few drops of dilute sulphuric acid. After remaining some time it is filtered and the filtrate mixed with three times its volume of alcohol. If there is any precipitate it is sulphate of strontia, or possibly sulphate of lime, and must be kept. It may be called *x*.

The sulphate of baryta filtered off is washed and allowed to remain for twelve hours in contact with a concentrated solution of carbonate of ammonia in a separate funnel. The tap is then opened, the liquid allowed to run out, the precipitate washed and treated with very dilute nitric acid—this dissolves out any strontia present, which has now been converted into carbonate—and the residue after being washed is dried, ignited and weighed as pure sulphate of baryta. The nitric acid solution possibly containing strontia is kept. It may be called *y*.

The filtrate from the silica is largely diluted and treated warm with sulphuretted hydrogen to precipitate any metals of the fifth and sixth groups that may be in the solution,* and filtered; the filtrate is boiled with nitric acid, the iron precipitated as basic salt (§ 160 B. 3 *a*) and the filtrate supersaturated with ammonia. If a small precipitate is found in this way, it is freed from manganese by repeated solution in hydrochloric acid and precipitated with ammonia. The manganese is precipitated from the concentrated filtrate in the usual way by sulphide of ammonium† (see p. 154) and the lime, &c., in the filtrate from this are thrown down by ammonia and carbonate of ammonia. If the alumina has not been determined in 3, the large precipitate obtained by basic precipitation, is used along with the small precipitate produced by ammonia (consisting chiefly of ferric oxide, but which contains the alumina and the residue of the silica, and also titanic acid if present). The alumina is determined by the methods given in 3 (p. 154).

The precipitate, consisting chiefly of carbonate of lime, is collected, washed and dissolved in nitric acid. The above-mentioned solution *y* which may contain strontia is added, and the whole evaporated to dryness—finally, in a flask heated on a sand bath, the moist air being removed by means of a water pump. The residue is then treated with ether-alcohol, not too large a quantity, to dissolve the nitrate of lime.

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* If there is any precipitate, care must be taken to ascertain if the metal is derived from the pan in which the water was evaporated.

† If the sulphide of ammonium precipitate is dark coloured it may contain nickel or cobalt, zinc also may be present; their separation may be effected according to § 160, B. 6.

The residue insoluble in the ether-alcohol is dissolved in water (if any remains undissolved it must be incinerated and examined spectroscopically), and after being evaporated to a small bulk is mixed with excess of a concentrated solution of sulphate of ammonia (1 : 4) and allowed to remain for 12 hours.

First of all, the above-mentioned precipitate x (if any) is collected on a small filter; then that produced by the sulphate of ammonia. It is advisable to close the funnel at first at the bottom, that the sulphate of ammonia may dissolve any sulphate of lime there may be in x. The precipitate is washed with sulphate of ammonia solution until the washings are no longer rendered turbid by oxalate of ammonia, and the sulphate of strontia is then dried and weighed. After being weighed, it must be examined spectroscopically.

7. Estimation of the Phosphoric Acid.

The estimation of the phosphoric acid may be combined with that of the iron, alumina, &c., in 3, or in the portion 6, but the best way is to take a separate bottle of the water (about 6 litres) for the purpose. This is evaporated with hydrochloric acid, the silica separated, and the filtrate repeatedly evaporated with nitric acid almost to dryness; the residue is then dissolved in nitric acid and water, precipitated with a nitric acid solution of molybdate of ammonia, and the phosphoric acid finally determined as pyrophosphate of magnesia (§ 134, 1 *b*, *β*).

8. Estimation of the Ammonia.

To effect the estimation of the ammonia, the author usually employs the following method :—

About 2000 grams of the mineral water, with addition of a small measured amount of dilute hydrochloric acid, is evaporated to a small bulk with the greatest care in a tubulated retort. To this, a measured quantity of freshly prepared solution of soda is added through a funnel-tube, the neck of the retort being inclined a little upwards, and the contents kept boiling until the liquid is almost entirely evaporated. The whole of the escaping vapours are passed into a Liebig's condenser, and the distillate is received in a tubulated receiver containing a little water acidified with a small measured quantity of hydrochloric acid, the tubulure being connected with a U-tube containing some water. The chloride of ammonium contained in the receivers is then converted into platinochloride by evaporation with a measured quantity of bichloride of platinum (§ 99, 2). A control experiment is made with the same quantities of hydrochloric acid, bichloride of platinum, and spirit; and the small amount of platinochloride of ammonium thus obtained is deducted from that found in the first experiment: the difference gives the quantity in the water with great exactness.

Instead of this method, the more simple process which BOUSSINGAULT* has proposed may be employed with the most satisfactory results. It is conducted as follows :—

About 10 litres of the water are boiled in a distilling apparatus until about $\frac{2}{5}$ have passed over; with saline waters, some solution of soda or milk of lime must be added so as to insure the whole of the ammonia passing over; the distillate is then transferred to a flask connected with a Liebig's condenser, and $\frac{1}{5}$ distilled over. The ammonia is determined in this distillate by adding 5 or 10 c. c. of very dilute sulphuric acid, and saturating the excess of the latter by a solution of soda, of which 5 c. c. neutralize 1 c. c. of the sulphuric acid (comp. § 99, 3). Another $\frac{1}{5}$ is distilled over, and the ammonia in this (if any is still present) is determined in the same way. But the first portion usually contains the whole of the ammonia.

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* Compt. rend. 36, 814; Pharm. Centralblatt, 1853, 369.

9. Estimation of the Nitric Acid.

The estimation of the nitric acid in mineral waters is conducted in precisely the same way as in spring-water § 205, 3 (p. 116).

10. Detection and Estimation of the Crenic and Apocrenic Acids.

A rather large quantity of the precipitate formed on the evaporation of the water, is boiled for about 1 hour with potash solution; filtered, acidified with acetic acid, and ammonia added; after 12 hours, the precipitate of silicic acid and alumina, which usually forms, is filtered off. To the filtrate, acetic acid is added to acid reaction, and then neutral acetate of copper. If a brownish precipitate is formed, this consists of apocrenate of copper (which, according to MULDER, contains variable quantities of ammonia; dried at 140° it gave 42·8 per cent. of oxide of copper). The liquid filtered from the precipitate is mixed with carbonate of ammonia, until the green colour is changed to blue, and a gentle heat applied. If a bluish-green precipitate forms, this is crenate of copper, which, dried at 140°, contains 74·12 per cent. of oxide of copper (MULDER).*

11. Detection and Estimation of Volatile Organic Acids.

SCHERER† found, in his analysis of the mineral spring of Brückenau, in Bavaria, also butyric acid, propionic acid, acetic acid, and formic acid—substances which had not before been observed in mineral waters. Soon after, the author also found traces of the same acids in the sulphur spring of Weilbach.‡ If it is intended to examine a mineral water for these acids, the water must be used quite fresh, as otherwise the acids in question might be produced by decomposition subsequent to collection. The following is SCHERER's process for determining these acids:—

A rather large quantity of the mineral water is evaporated and filtered from the precipitate formed. If the water contains no alkaline bicarbonate, carbonate of soda is added to alkaline reaction, before proceeding to evaporate. The concentrated mother-liquor is cautiously acidified with sulphuric acid, and the chlorine precipitated by sulphate of silver, taking care to have rather a trace of chlorine than of silver in excess. It is then filtered and the filtrate distilled until the fluid passing over no longer shows an acid reaction, the distillate is saturated with baryta water, and any excess of baryta removed by carbonic acid.

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* For more detailed information on the subject of crenic acid and apocrenic acid, consult MULDER (Journ. f. prakt. Chem. 32, 321; Chem. Gaz., 3, 1).

† Annal. d. Chem. u. Pharm. 99, 257.

‡ Journ. f. prakt. Chem. 70, 15.

The liquid is then boiled, concentrated, filtered, evaporated to dryness in a weighed dish, dried at 100°, and the residue, which contains the volatile organic acids in combination with baryta, is weighed. The residue is then extracted with warm spirit of wine, which leaves the formate of baryta undissolved. After the latter is dried and weighed, it should be tested with solution of nitrate of silver and with chloride of mercury.* The alcoholic solution of the other baryta compounds is evaporated at a gentle heat, the larger portion of the residue dissolved in a copious amount of water, and the baryta precipitated from the solution by sulphate of silver, with proper precautions. The liquid filtered from the precipitate is allowed to evaporate under the desiccator. As soon as a sufficient quantity of silver salt has crystallized, the crystals are separated from the liquid, dried over sulphuric acid, and the dry salt employed for the determination of the equivalent. Finally, the rest of the liquid is allowed to evaporate over sulphuric acid, the salt pressed between sheets of blotting paper, dried over sulphuric acid, and analysed.

By way of control, the baryta in another portion of the residue left on evaporation of the alcoholic solution of the baryta salts is determined by means of sulphuric acid. In this process, the peculiar odour of the volatile fatty acids (propionic, butyric, &c.) may be recognised. If the fluid is sufficiently concentrated, and has been allowed to stand at rest for some time, the microscope will occasionally show minute fatty drops floating on the surface.

If the traces of volatile organic acids are very small and the quantity of metallic chlorides large, the precipitation of the chlorides by means of sulphate of silver, as in SCHERER's method, cannot be carried out, or only with very great difficulty. This occurred to the author in the examination of the Grindbrunnen, Frankfurt. A modification of SCHERER's process had to be employed, which is recommended in similar cases.† A large quantity of the water is evaporated —with addition of carbonate of soda if necessary—to a small bulk, the strongly alkaline liquid is filtered, dilute sulphuric acid added until the solution is neutral or slightly acid; and the slightly acid liquid is distilled down in a retort to a small volume. The somewhat acid distillate is neutralized with baryta, evaporated to dryness, and the residue heated with absolute alcohol. The solution is evaporated and the residue again treated with absolute alcohol. In this way the more easily soluble baryta salts of propionic acid, butyric acid, &c., are obtained on again evaporating the alcohol, whilst the sparingly soluble formate of baryta can be extracted from the residue by water.‡

12. Estimation of other Organic Compounds (Resins) Extractive Matters.

Other organic substances may be present in mineral waters besides those mentioned in 10 and 11. Those which are dissolved out by alcohol, when the residue left on the evaporation of a mineral water is treated with that solvent, are as a rule of a resinous nature. Others are insoluble in alcohol but may be dissolved out by water; these are usually called extractive matters for want of a better name. Sometimes also small quantities of organic matter remain in the residue after it has been extracted with alcohol and water. These are products of decomposition which have been formed during the evaporation.

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* The operator should remember that the formate of baryta may contain nitrate of baryta.

† Zeitschr. f. anal. Chem. 14, 323.

‡ One hundred grams boiling absolute alcohol dissolve 0·0055 gram formate, 0·0284 gram acetate, 0·2610 gram propionate, and 1·1717 gram butyrate of baryta (E. LUCK, Zeitschr. f. anal. Chem. 10, 185).

If the resinous or extractive matters are to be tested for or accurately determined, it is above all things necessary that the water shall not come in contact with cork or caoutchouc, or be contaminated with dust during the evaporation; pure alcohol too must be used, it should not leave the slightest residue on evaporation. If these precautions are not observed, resinous or extractive matters may be found which do not owe their origin to the mineral water.

The author used the following method* for the determination of these organic substances in the Grindbrunnen water at Frankfurt, and recommends it in similar cases.

A larger volume of the water (10—20 litres) is evaporated with the strictest regard to cleanliness, and finally, with the greatest care, is taken down to complete dryness, the residue being extracted with *pure* absolute alcohol. In this way a solution *a* and a residue *b* are obtained. The alcohol is distilled off from the solution *a*, the residue is treated with water, in which the greater part of it will dissolve, and then filtered through a small asbestos filter. If any trace of resin remains on the filter, it is washed with water, dried and dissolved in absolute alcohol; this solution is evaporated in a weighed platinum dish, the residue weighed, heated, and the odour noted; the incombustible residue is weighed, and the difference between the two weights is entered as resin. The aqueous solution, filtered from the resin, is added to the residue *b*, and the whole extracted with water; the solution is acidified with dilute sulphuric acid and gently heated for some time to drive off all the carbonic acid. It is then evaporated down to dryness with the addition of freshly ignited oxide of lead *perfectly free from carbonate;* the residue is mixed with an excess of chromate of lead and a combustion made (§ 176). The humus-like substance is calculated from the carbon with comparative accuracy by reckoning, according to FR. SCHULZE,† 100 parts of humus-like substance for 58 parts of carbon.

The residue, which is insoluble in alcohol and water, is treated with dilute hydrochloric acid. If a residue containing organic matter is left it is collected on an asbestos filter, washed, burnt with chromate of lead (§ 176), and the insoluble humus-like substance calculated from the carbonic acid.

13. Examination of the Gases.

§ 210.

The following method is employed for the examination of the gases collected at the spring, and brought to the laboratory in sealed tubes, whether they were expelled from the water by boiling (§ 208, 10, *a*, or *b*), or whether they were spontaneously disengaged from the spring (§ 208, 11). A graduated tube of the form described Vol. I. p. 21, and illustrated in fig. 4, is moistened inside with a drop of water, and then filled with mercury;* the tube containing the gas is immersed in the mercurial trough, the point broken off, and, by giving the proper inclination, the gas is caused to ascend into the graduated tube. The volume of the gas is then read off, noting the temperature and atmospheric pressure, and a ball of hydrate of potassa moistened with water,† is introduced into the gas by means of a platinum wire, on which it is cast. Care must be taken not to allow the other end of the wire to project above the surface of the mercury, otherwise diffusion of the confined gas with the atmospheric air will take place along the wire. When the volume of the gas shows no further diminution, the moist potash ball is replaced by another, and finally, when absorption has ceased, the second moist ball is again replaced by a dry one, this also is removed after an hour, and the volume of the gas is then read off. The gas absorbed consists of carbonic acid, and, in cases where sulphuretted hydrogen is present, also of the latter gas, which, however, has already been determined; still, the sulphide of potassium in the potassa ball may be estimated as directed Vol. I. p. 388, *B*, *a*.

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* Zeitschr. f anal. Chem. 14, 323.

† Journ. f. prakt. Chem. 47, 241.

The gaseous residue usually consists of oxygen and nitrogen only, in which case it may be examined as directed in the chapter on the Analysis of Atmospheric Air (§ 276). If there is reason to suspect the presence of marsh gas, the oxygen is removed next. This is effected most conveniently by means of a ball of papier-maché fixed on the end of a platinum wire and moistened with a concentrated alkaline solution of pyrogallate of potassa; after some time, this may be replaced, if necessary, by a second ball; the gas is then dried by a ball of hydrate of potassa (Bunsen). The composition of the gaseous residue,‡ which generally consists either of nitrogen alone, or of nitrogen and marsh gas, is now ascertained by transferring it, wholly or partially, to a eudiometer (Vol. I. p. 22, fig. 3), mixing it with 8—12 vols. of air and 2 vols. of oxygen—to guard against the formation of nitric acid—and trying to explode the gaseous mixture. If this fails, electrolytic detonating gas is added until the mixture becomes explosive, the carbonic acid generated is re-absorbed, the marsh gas calculated from this, and the nitrogen estimated by difference. For the details of the process, the student is referred to Bunsen's "Gasometry," a work which ought to be in the hands of every one engaged in gas analysis.

To ascertain whether the gaseous residue left after the absorption of the carbonic acid and oxygen, contains carburetted hydrogen, and also to determine it, the following method may often be successfully employed:—One limb of a narrow U-tube is inserted into the cylinder containing the gaseous residue, which is confined over water, whilst the other limb is connected with a piece of India-rubber tubing, closed by a clip.

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* See p. 38, foot-note.

† Which, besides the water of hydration, contains also water of crystallization. Balls of this kind are made by pouring fused crystallized hydrate of potassa into a bullet-mould of about six mm. inner diameter, into which a platinum wire is inserted, with the end reaching into the middle. After cooling, the ball is found attached to the wire. The neck which has formed on the wire may be removed with a knife.

‡ If the gas contains but little oxygen there is no fear that any appreciable trace of carbonic oxide will be formed by the pyrogallate of potassa, but if much oxygen is present, it is necessary—in order to avoid error—to test another portion of the original gas (from which the carbonic acid has been removed but not the oxygen) for hydrocarbons (Boussingault, Calvert, Cloëz, Poleck, Zeitschr. f. anal. Chem. 3, 347, and 8, 451).

An apparatus is then arranged in the following manner:—some solution of potassa is poured into a small U-tube, the outer limb of which is furnished with a little tube bent at a right angle, closed by a small piece of India-rubber tubing and a screw clip. The other limb is connected with a second small U-tube, filled with soda-lime, and this again with a thin piece of combustion tube, 20 cm. long, filled in the middle with a rather closely packed layer, about 8 cm. long, of fine copper turnings strongly oxidized by ignition in oxygen gas. The other end of the combustion tube is connected with a somewhat larger U-tube, containing baryta water, this again with a potash tube, and the latter with an aspirator. The cock of the latter is opened, so as to see whether the joinings are air-tight, the copper turnings are heated to redness, by means of two gas lamps, the screw clip cautiously opened, and a slow current of air passed through the apparatus for five minutes. This should not impart the least turbidity to the baryta water; if the baryta water is rendered turbid, it must be replaced by a fresh portion, after the first ignition, and the experiment repeated. If the baryta water remains clear, the India-rubber tube, which is closed by a plain clip, is connected by means of a small glass tube, with that provided with a screw-clip. As the former, which closes the U-tube leading to the cylinder, remains closed, no more air bubbles can pass through the apparatus. The clip is now opened a little, and the gas of the cylinder allowed to enter very slowly. The quantity of gas is generally so small that it remains entirely in the first U-tube. When all the gas is drawn in, some water is allowed to enter, and the clip closed only when the water just makes its appearance in the little glass tube behind it. The screw-clip is now closed, the India-rubber tube with the plain clip disconnected, and, opening the screw-clip a little, a very slow current of pure air taken from the open and filtered through cotton-wool is allowed to pass for a sufficient length of time over the red-hot oxide of copper. This current of air carries with it the gas which has previously entered; if this contains carburetted hydrogen, the baryta water is rendered turbid, owing to the formation of carbonate of baryta. If the turbidity is sufficiently marked, the quantity of the carbonate of baryta may be determined, and the amount of marsh gas calculated from the result. If the carbonic acid is to be collected in a soda-lime tube, the apparatus described by the author* should be used.

MODIFICATIONS REQUIRED WITH SALINE WATERS, THAT IS, WITH WATERS WHICH DO NOT CONTAIN ALKALINE BICARBONATE.

§ 211.

1. Determination of the total amount of the fixed constituents.

If the total amount of the fixed constituents is determined by the method already given § 209, 1, there is a slight loss of chloride of magnesium, since a portion of it is decomposed by the water during evaporation, hydrochloric acid being given off and magnesia remaining.

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* Zeitschr. f. anal. Chem. 3, 340.

As a rule, however, the error is scarcely appreciable and may generally be disregarded, especially as the total of the salts found by direct evaporation never agrees accurately with the total constituents determined directly, from causes which have been already explained § 205, I. 9. The best way to avoid this source of error is to adopt F. MOHR's suggestion and evaporate down the water with a weighed quantity of ignited carbonate of soda, or by TILLMANN's method,* with the addition of a known quantity of sulphate of potash. In the latter case, MgCl and $2(KO,SO_3)$ are resolved into the double salt $KO,SO_3 + MgO,SO_3$ and KCl.

2. Determination of the Lime and Magnesia.

If a mineral water contains alkaline carbonates there can be no soluble salt of lime or magnesia; but all lime and magnesia found must be considered as carbonate dissolved by means of carbonic acid, even when all the lime is not precipitated on heating the water; this observation applies with even greater force to the magnesia. With saline waters the case is different. These almost always contain carbonate of lime and carbonate of magnesia besides soluble lime and magnesia salts. In order to determine in saline waters in what proportions the two bases are combined with carbonic acid and with other acids, it is necessary, in addition to the determination of the total lime, &c., according to § 209, 3, to make a separate determination of the lime remaining in solution after boiling; the proportions in which the magnesia is combined with carbonic acid and with other acids can then be calculated† (see § 213).

A flask of the capacity of about 1500 c. c. is tared and weighed, 1000 grams of the mineral water are poured in and boiled for an hour, the water which evaporates being replaced at intervals by distilled water. When quite cold, the flask is weighed with its contents, and on subtracting the weight of the empty flask the weight of the boiled liquid is known. It is then filtered through a dry filter without washing the precipitate, the filtrate is weighed, the lime contained in it is determined by a double precipitation with oxalate of ammonia, as in § 209, 3, and the quantity of lime remaining dissolved in the 1000 grams of mineral water is calculated from the consideration:—the amount of lime in the weighed quantity of the liquid obtained by filtering off the precipitate through a dry filter being known, how much would the total liquid (which contains the lime in 1000 grams of the mineral water remaining dissolved) as weighed after cooling, give?

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* Anal. der Chem. u. Pharm. 81, 369.

† The earlier method of determining the lime precipitated by boiling and that which remains dissolved consisted in filtering the boiled water, thoroughly washing the precipitate with water, and making determinations of the lime in the precipitate and in the filtrate; this is omitted here and replaced by the method above described. It is easy to understand that by either method the lime in the solution must be too high, and the lime in the precipitate too low, for not only does the small quantity of chloride of ammonium which is generally present in saline waters react with the carbonate of lime on boiling, but carbonate of lime is not quite insoluble in water. The latter error is naturally greater if the precipitated carbonate of lime is washed.—Under these circumstances, the correction given in the method described in the text may be neglected, as the water after boiling contains some suspended carbonate of lime, so that its influence on the result is hardly appreciable and quite within the limits of unavoidable error. The determination, as to how much of the magnesia is combined with carbonic acid, and how much with hydrochloric acid, sulphuric acid, &c., cannot be performed accurately by boiling the water and estimating the magnesia in the filtrate and in the precipitate; besides, it is unnecessary, as the calculation of the analysis gives the desired result. In waters containing sulphate of lime, this is not the case with certainty, because—as E. BOHLIG (Pharm. Centralb. 18, 430) has pointed out—bicarbonate of magnesia and sulphate of lime are decomposed, by boiling, into sulphate of magnesia, carbonate of lime and carbonic acid. According to the author's experiments this decomposition does not occur in waters rich in sulphate of magnesia.

If this determination is performed twice, it will yield entirely concordant results. That they are rather too high, in consequence of the solubility of carbonate of lime in water, is an error which cannot be avoided. A correction can indeed be made, as it is known that 28,500 parts of water dissolve 1 part of carbonate of lime (Vol. I. p. 122). This correction ought to be made, although it cannot lay claim to great accuracy, as the various soluble salts contained in the mineral water have an appreciable influence on the solubility of the carbonate of lime, but one which it is difficult to estimate. As a rule, the greater part of the baryta and strontia are contained in the lime, which is estimated in the boiled water, whilst smaller quanties are precipitated as carbonate on boiling; indeed (this may be considered as very probable) in consequence of the bicarbonate of lime—in water containing chloride of sodium—reacting with the sulphates of baryta and strontia yielding carbonates of baryta and strontia, sulphate of lime and carbonic acid. On this account, the amount of lime remaining in solution appears to be slighly larger than it really is. If all the strontia and baryta originally present in the water are subtracted, as is usually done, from the lime (containing strontia and baryta) found in the boiled water, a slight error is evidently introduced, in consequence of the inequality of the atomic weights, for correctly, only so much of the strontia and baryta contained in the boiled water should be subtracted from or added to the lime as is equivalent to the strontia and baryta separated by boiling.

To avoid this small error, it is merely necessary to estimate the strontia and baryta in the lime (containing strontia and baryta) obtained from the boiled water and subtract their weight from the lime + strontia + baryta obtained from the boiled water, whilst on the other hand the amount of lime, which is equivalent to the small quantities of strontia and baryta, separated, on boiling, as carbonates along with the carbonate of lime, is added to the weight of lime thus found. These are estimated by subtracting the strontia and baryta in the boiled water from the total weights originally found.

These small corrections, however, are scarcely worth considering, from the circumstance that the bicarbonate of magnesia is decomposed by boiling with sulphate of lime. (See foot-note (†) p. 167.)

3. Determination of Iodine and Bromine.

With alkaline mineral waters, the evaporation (described in § 209, 6) of a large bulk can be performed without any addition and without fear of loss of iodine or bromine. With waters which are not alkaline, however, there is not the same security, as a portion of these halogens may be volatilized by the decomposition of the bromide and iodide of magnesium. It becomes necessary, therefore, to add to saline waters, enough perfectly pure (it is best to boil it repeatedly with alcohol) carbonate of soda to give a strongly alkaline reaction before evaporating the large quantity. The iodine and bromine, &c., can then be determined as directed in § 209, 6.

4. Determination of Baryta and Strontia.

No satisfactory clue as to the combinations in which baryta and strontia are contained in saline waters can be obtained from their behaviour on boiling. As a rule, part of the baryta and strontia is found in the precipitate, while the rest remains dissolved, and according as the one or the other appears to be larger in amount (approximate inferences can be drawn from spectroscopic observations) it has been customary to calculate the two bases either as sulphates or as carbonates. From the employment of these different ways of arranging the results, the analyses of mineral waters are not comparable; it would be best therefore to reckon the baryta and strontia, in saline waters, as sulphates. These are more soluble in water containing chloride of sodium than in pure water, therefore their occurrence—especially that of sulphate of baryta—in solution is not surprising, and their partial separation as carbonates on boiling the water is explained by the reaction of the bicarbonate of lime with these sulphates forming sulphate of lime and carbonates of baryta and strontia, as already noticed § 211, 2.

5. Estimation of the Ammonia, and detection and estimation of the Volatile Organic Acids.

Attention has already been drawn § 209, 8 and 11 (in brackets) to the slight modifications of Boussingault's method to be employed in estimating the ammonia and evaporating the mineral water, for the detection and estimation of volatile organic acids, if the waters contain no bicarbonate of soda.

Remarks on the Analysis of Sulphuretted Waters.

§ 212.

It has already been noticed (§ 208, 8) that the sulphur in sulphuretted waters may be present in different forms of combination, and the best methods for determining the free sulphuretted hydrogen, as well as the sulphuretted hydrogen existing in combination with a metallic sulphide, in the form of a sulpho-salt, have been described; also the sulphur present in the form of proto- or bisulphide, and, lastly, the hyposulphurous acid which may be present.

A few additional remarks may be inserted here:

1. The determination of the sulphuric acid cannot be effected in the usual way, as the sulphuretted hydrogen is constantly undergoing oxidation by the oxygen of the air, which must of necessity lead to serious errors. The estimation is made as in § 167.

2. The total amount of the sulphur, in whatever form of combination—whether with oxygen, hydrogen, or metals—is estimated, by way of control, by passing chlorine gas free from air into a measured quantity of the water, concentrating after addition of some hydrochloric acid, and precipitating the sulphuric acid formed with chloride of barium.

3. The deportment of mineral waters containing free sulphuretted hydrogen differs of course from that of waters containing principally metallic sulphides, or sulpho-salts (hepatic waters). The water of Weilbach may be taken as an illustration of waters of the *former description;* in this, nearly the whole of the sulphur which is not combined with oxygen is present as free sulphuretted hydrogen. The water smells strongly of this gas; when shaken in a half-filled bottle, it evolves sulphuretted hydrogen with the carbonic acid; on passing hydrogen through it, it almost entirely loses the sulphuretted hydrogen. When kept in a bottle containing air, sulphur soon separates, the liquid becoming turbid, and depositing a precipitate of sulphur, which by the action of the air is oxidized, and usually dissolves again, leaving the water as clear as at first.

The water of Stachelberg, analysed by SIMMLER,* may be taken as an illustration of waters of the *latter description.* This water has but a slight odour of sulphuretted hydrogen; and in winter scarcely any; red litmus paper is coloured blue by it in the course of a minute; but turmeric paper is not altered. Protochloride of manganese produces a flesh-coloured, and protosulphate of iron a black precipitate. Nitroprusside of sodium imparts to it a reddish violet tint. If a bottle is filled with the water, the latter soon begins to turn slightly turbid; after about five minutes it recovers its original clearness, but the colour is now distinctly yellowish. Upon further access of air, renewed turbidity and clearing takes place, and the water becomes deep yellow from formation of the bisulphide. With full access of air, there is a copious precipitation of sulphur and simultaneous formation of hyposulphite of soda.

The cause of the different behaviour of these two kinds of sulphuretted water becomes apparent on considering the different proportion which the sulphur, in combination with hydrogen or metals, bears to the free carbonic acid in the two waters; this proportion is 1 : 24 in the water of Weilbach, and 1 : 2 in that of Stachelberg. If a current of carbonic acid were passed into the latter, this would convert the hepatic water into a water containing free sulphuretted hydrogen; since carbonic acid expels sulphuretted hydrogen from sulphide of sodium or hydrosulphide of sodium, as, on the other hand, sulphuretted hydrogen expels carbonic acid from bicarbonate of soda.

Owing to these slight differences of affinity, the action depends on the amount of either compound present; the larger, therefore, the amount of free carbonic acid in a water containing carbonate of soda, the smaller will be the quantity of sulphuretted hydrogen in a state of combination, and the larger that of free sulphuretted hydrogen. The temperature also has some influence in the matter; thus, for instance, bicarbonate of soda may exist in the cold in the presence of sulphide of sodium, whilst at a higher temperature monocarbonate will form, with disengagement of sulphuretted hydrogen. Sulphuretted waters containing no alkaline bicarbonates, and accordingly acquire no alkaline reaction after being boiled, may be regarded as simple solutions of sulphuretted hydrogen; the sulphuretted water of Sandefjord, analysed by A. and H. STRECKER,† belongs to this class.

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* Journ. f. prakt. Chem. 71, 1.

† Anal. d. Chem. u. Pharm. 95, 175.

2. Calculation, Control, and Arrangement of the Results of Analyses of Mineral Waters.

§ 213.

The results of the several analytical processes described in 1, are obtained by direct experiment, and are altogether independent of any theoretical views which may be entertained as to the manner in which the several constituents are combined or associated with each other. As our theoretical views on the subject may change with the progress of chemistry, it is absolutely indispensable, in reports of analyses of waters, to give the direct results and the methods by which they were obtained. It is then of service for all time, as it supplies, at least, the requisite data for determining whether the composition of a water is constant or not.

With respect to the principles that guide chemists in the hypothetical association of the acids and bases found in the water, it is assumed that the combination of the bases and acids is governed by their respective affinities, that is, the strongest acid is assumed to be combined with the strongest base, &c.; due attention being paid, however, also, to the greater or less degree of solubility of the salts, since it is well known that this exercises a considerable influence on the manifestations of the force of affinity. Thus, for instance, when lime, potassa, and sulphuric acid are found in the boiled water, the sulphuric acid is assumed to exist, in the first place, in combination with the lime, &c. It cannot be denied, however, that in this way much is left to the individual views and discretion of the analyst, and, consequently, that different reports might be calculated from the very same set of experimental results.

A general understanding upon this point would be very advantageous, because without it the comparison of two mineral waters is beset with difficulties. As long as an agreement of this kind is wanting, a comparison between two mineral waters can only be made as regards the direct and immediate results of the respective analyses.

One point, however, should be at once agreed upon, namely, to put all the salts down in the anhydrous condition.

The Elisabethenquelle at Homburg, v. d. Höhe, analysed by the author, is chosen as an example to illustrate as clearly as possible the basis of the most correct arrangement, and also the method by which the results may be controlled. The water is saline. This class of water has been selected because its calculation is somewhat complicated. In the case of alkaline waters, the arrangement is simpler, since in these it is usual to calculate all alkaline earths as carbonates or bicarbonates.

Analysis of the Water of the Elisabethenquelle at Homburg, v. d. Höhe.

a. Direct Results of the Analysis.

The numbers express the mean of two or three concordant experiments, and give the weight in grams of substance in 1000 grams of the water.

1. Chloride, bromide and iodide of silver together		28·97763
2. Bromine and iodine—		
a. Bromine		0·002486
Corresponding with bromide of silver		0·00584
b. Iodine		0·0000285
Corresponding with iodide of silver		0·000053
3. Chlorine—		
Chloride, bromide and iodide of silver		28·97763
Deduct—		
Bromide of silver	0·00584	
Iodide of silver	0·00005	0·00589
Remainder, chloride of silver		28·97174
Corresponding with chlorine		7·16264
4. Sulphuric acid		0·01796
5. Carbonic acid (total)		3·32925
6. Silicic acid		0·02635
7. Protoxide of iron		0·01438
8. Lime and strontia together, expressed as carbonates		2·15885
9. Magnesia (total)		0·32129
10. Lime and strontia * retained in solution after boiling the water, expressed as carbonates		0·64633
11. Lime precipitated on boiling—		
Total lime + strontia, expressed as carbonates		2·15885
Lime and strontia retained in solution on boiling, expressed as carbonates		0·64633
The remainder =		1·51252
Gives in form of carbonate the amount of lime precipitated on boiling; this corresponds with lime.		0·84701
12. Lime retained in solution after boiling—		
Sum of the lime and strontia retained in solution, expressed as carbonates		0·64633
Deduct the strontia (see 13), which calculated into carbonate =		0·01428
Remainder =		0·63205
Which corresponds with lime		0·35395
13. Baryta, strontia, and protoxide of manganese—		
a. Baryta		0·00066
b. Strontia		0·01002
c. Protoxide of manganese		0·00094

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* All the strontia was retained in solution, the trace of baryta which was within the limits of the experimental error in the lime determination was neglected in *this* calculation.

14. Phosphoric acid		0·00043
15. Lithia		0·00764
Corresponding with chloride of lithium		0·02163
16. Chloride of sodium + chloride of potassium + chloride of lithium		10·22880
17. Potash		0·21876
Corresponding with chloride of potassium		0·34627
18. Soda—		
Sum of the chlorides of sodium, potassium and lithium		10·22880
Deduct—		
Chloride of potassium	0·34627	
Chloride of lithium	0·02163	0·36790
Remainder, chloride of sodium		9·86090
Which corresponds with soda		5·22899
19. Oxide of ammonium		0·010655
20. Total of fixed constituents		13·18438
21. Specific gravity	1·01140 at 19·5°	

The following substances were present in unweighable amounts, viz., cæsia, rubidia, alumina, protoxide of nickel, protoxide of cobalt, oxide of copper, teroxide of antimony, arsenic acid, boracic acid, fluorine, nitric acid, volatile organic acids, non-volatile organic matter, nitrogen, light carburetted hydrogen, sulphuretted hydrogen.

b. Calculation.

a. Sulphate of baryta—		
Baryta present (13)		0·00066
Combines with sulphuric acid		0·00034
To form sulphate of baryta		0·00100
b. Sulphate of strontia—		
Strontia present (13)		0·01002
Combines with sulphuric acid		0·00774
To form sulphate of strontia		0·01776
c. Sulphate of lime—		
Sulphuric acid present (4)		0·01796
Of this is combined—		
With baryta	0·00034	
With strontia	0·00774	0·00808
The remainder		0·00988
Combines with lime		0·00692
To form sulphate of lime		0·01680
d. Bromide of magnesium—		
Bromine present (2)		0·002486
Combines with magnesium		0·000373
To form bromide of magnesium		0·002859

e. Iodide of magnesium—

Iodide present (2)	0·0000285
Combines with magnesium	0·0000027
To form iodide of magnesium	0·0000312

f. Chloride of calcium—

Lime present in boiled water (12)	0·35395
Of which is combined with sulphuric acid (*c*)	0·00692
The remainder	0·34703
Corresponds with calcium	0·24788
Which combines with chlorine	0·43949
To form chloride of calcium	0·68737

g. Chloride of potassium—

Potash present (17)	0·21876
Corresponds with potassium	0·18161
Which combines with chlorine	0·16466
To form chloride of potassium	0·34627

h. Chloride of lithium—

Lithia present (15)	0·00764
Corresponds with lithium	0·00356
Which combines with chlorine	0·01807
To form chloride of lithium	0·02163

i. Chloride of ammonium—

Oxide of ammonium present (19)	0·01065
Corresponds with ammonium	0·00737
Which combines with chlorine	0·01452
To form chloride of ammonium	0·02189

k. Chloride of sodium—

Soda present (18)	5·22899
Corresponds with sodium	3·87957
Which combines with chlorine	5·98133
To form chloride of sodium	9·86090

l. Chloride of magnesium—

Chlorine present (3)		7·16264
Of this is combined—		
With calcium	0·43949	
With potassium	0·16466	
With lithium	0·01807	
With ammonium	0·01452	
With sodium	5·98133	6·61807
Remainder		0·54457
Which combines with magnesium		0·18429
To form chloride of magnesium		0·72886

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m. Phosphate of lime—		
Phosphoric acid present (14)		0·00043
Combines with lime (3 eq.)		0·00051
To form basic phosphate of lime		0·00094
n. Carbonate of lime—		
Lime present in precipitate obtained by boiling (11)		0·84701
Of this is combined with phosphoric acid (*m*)		0·00051
The remainder		0·84650
Combines with carbonic acid		0·66511
To form monocarbonate of lime		1·51161
o. Carbonate of magnesia—		
Total magnesia (9)		0·32129
Corresponds with magnesium		0·19277
Of which is combined—		
With bromine (*d*)	0·000373	
With iodine (*e*)	0·000003	
With chlorine (*l*)	0·184290	0·18467
The remainder		0·00810
Corresponds to magnesia		0·01350
Which combines with carbonic acid		0·01485
To form monocarbonate of magnesia		0·02835
p. Protocarbonate of iron—		
Protoxide of iron present (7)		0·01438
Combines with carbonic acid		0·00879
To form protocarbonate of iron		0·02317
q. Protocarbonate of manganese—		
Protoxide of manganese present (13)		0·00094
Combines with carbonic acid		0·00058
To form protocarbonate of manganese		0·00152
r. Silicic acid—		
Silicic acid present (6)		0·02635
s. Free carbonic acid—		
Total carbonic acid (5)		3·32925
Of this is combined to form neutral salts—		
With lime (*n*)	0·66511	
With magnesia (*o*)	0·01485	
With protoxide of iron (*p*)	0·00879	
With protoxide of manganese (*q*)	0·00058	0·68933
Remainder		2·63992
Of this is combined with monocarbonates forming bicarbonates		0·68933
Remainder, free carbonic acid		1·95059

c. Comparison of the total amount of fixed Constituents found directly with the sum of the several Constituents.

The several determinations have given—

Sulphate of baryta	0·00100
Sulphate of strontia	0·01776
Sulphate of lime	0·01680
Bromide of magnesium	0·00286
Iodide of magnesium	0·00003
Chloride of calcium	0·68737
Chloride of potassium	0·34627
Chloride of lithium	0·02163
Chloride of ammonium	0·02189
Chloride of sodium	9·86090
Chloride of magnesium	0·72886
Phosphate of lime	0·00094
Carbonate of lime	1·51161
Carbonate of magnesia	0·02835
Sesquioxide of iron*	0·01598
Protosesquioxide of manganese*	0·00101
Silicic acid	0·02635
	13·28961
The residue dried at 180°	13·18438

It is not to be expected that these numbers will correspond exactly, especially in the case of a water like the above; in fact, if they did agree with each other, we should have good reason for inferring that the analysis was incorrect. The causes of the difference are manifest, although they can scarcely be expressed numerically. Firstly, the chloride of ammonium is decomposed on evaporation with carbonate of lime, carbonate of ammonium escaping, and chloride of calcium being found; then the chloride, bromide and iodide of magnesium become basic with loss of a portion of their respective hydrogen acids; again silicic acid expels carbonic acid when evaporated with carbonates. All these causes, too, tend in one direction, causing the sum of the severally determined fixed constituents to be higher than that of the residue left on evaporation.

A more accurate control can be obtained by treating with sulphuric acid the residue left on evaporation (p. 152), and comparing the residue of the sulphates (the iron is present as sesquioxide) with the sum of the fixed alkalies, alkaline earths and manganese expressed as sulphates + the sesquioxide of iron, the silicic acid, also the alumina or phosphate of alumina present as such and—in alkaline waters—sometimes additional phosphoric acid as pyrophosphate of soda (in saline waters as phosphate of lime), and from the sum the amount of sulphate of soda (as sulphate of lime) corresponding with the pyrophosphate of soda (or phosphate of lime) is subtracted.

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* These compounds are here put down in the condition in which they are present in the residue dried at 180°.

As an example the author gives the control relating to his analysis of the Kränchen water at Ems.*

Below, the residue obtained by evaporation with sulphuric acid and gentle ignition is compared with the sum of the individual constituents calculated as sulphates in proportion to the oxides, &c., both results being given in parts per thousand.

Found soda 1·355391 calculated as sulphate of soda .	3·102042
„ potassa 0·019891 calculated as sulphate of potash	0·036773
„ lithia 0·001029 calculated as sulphate of lithia .	0·003769
„ lime 0·084068 calculated as sulphate of lime. .	0·204165
„ strontia 0·001266 calculated as sulphate of strontia.	0·002245
„ baryta 0·0006513 calculated as sulphate of baryta	0·000992
„ magnesia 0·064683 calculated as sulphate of magnesia	0·194050
„ protoxide of iron 0·000895 calculated as peroxide of iron	0·000994
„ protoxide of manganese 0·0000773 calculated as sulphate of manganese.	0·000164
„ silica calculated as silica	0·049741
„ phosphate of alumina	0·000116
„ phosphoric acid remaining 0·000367 calculated as pyrophosphate of soda	0·001367
	3·596418
Subtract sulphate of soda for phosphate of soda	0·001459
Sulphates, &c., remaining	3·594959
Direct determination . .	3·594699

d. Arrangement of the Results.

In reporting the water, the quantities of the ingredients may be represented in two ways—in parts per 1000 (or 1,000,000), and in grains per gallon (this vol. p. 132).

The most appropriate way of classifying the several constituents is as follows :—

a. Present in weighable quantity.
b. Present in unweighable quantity.

As regards the carbonates, it is a question whether they should be put down as neutral salts, the excess of carbonic acid being considered partly as forming bicarbonates, and partly as free acid; or whether they should be calculated at once as bicarbonates, the excess of the carbonic acid being then put down as present in the free state. Chemists sometimes adopt the first way, sometimes the second. The author generally reports his analyses of mineral waters both ways, to facilitate comparison with the analyses of those of similar springs.

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* Jahrb. d. Nassauischen Vereins f. Naturkunde, Jahrg. 27 and 28, pp. 114 *et seq.*

It is also usual to give the volume of the carbonic acid (and of the gases generally), calculated to the temperature of the spring and the normal pressure (760mm.). This is done in the first column in c. c. per litre; in the second, in cubic inches per gallon.

For further examples of the method of calculating and controlling, and of reporting the results, the following memoirs may be cited:—

1. Analysis of the Kochbrunnen of Wiesbaden (saline thermal spring).
2. Analysis of the mineral springs of Ems (thermal alkaline springs).
3. Analysis of the springs of Schlangenbad (thermal springs holding only an extremely small quantity of solid constituents in solution).
4. Analysis of the mineral springs of Langenschwalbach (alkaline chalybeate springs, abounding in carbonic acid).
5. Analysis of the sulphuretted springs of Weilbach (cold sulphuretted spring).
6. Analysis of the mineral spring of Geilnau (alkaline chalybeate spring, abounding in carbonic acid).
7. Analysis of the new soda spring of Weilbach (alkaline springs containing much lithia).
8. Analysis of the mineral spring at Niederselters (alkaline spring abounding in carbonic acid).
9. Analysis of the mineral spring at Fachingen (very rich in bicarbonate of soda).

All these papers are comprised in one work, entitled "Chemische Untersuchung der wichtigsten Mineralwasser des Herzogthums Nassau, von Professor Dr. R. Fresenius" (C. W. Kreidel, Wiesbaden). They will also be found in the "Jahrbücher des nassauischen naturhistorischen Vereins," Nos. 4, 5, and 6 are also published in the "Journal für praktische Chemie," Band 64, 70, 72.

Nos. 1 and 2 contain a detailed description of the methods employed in the examination of the muddy ochreous deposits and solid sinter-deposits of the springs in question.

The student may also consult the author's "Analyses of the Homburg Mineral Springs" (Kreidel, Wiesbaden)—these springs abound in carbonic acid, contain iron, and are very saline—and "Analysis of the Mineral Springs at Wildungen" (Mittler, Arolsen)—this water abounds in carbonic acid, is more or less alkaline and chalybeate, and contains much alkaline earthy bicarbonate.

The following are examples of analyses of mineral waters more recently made by the author:—

Trinkquelle, Badequelle and Helenenquelle at Pyrmont[1] (chalybeate springs containing much sulphate of lime).

Trinkquelle at Driburg (chalybeate spring containing much sulphate of lime), Hersler mineral spring (earthy mineral spring), also Satzer sulphuretted mud spring.[2]

Tönnissteiner Heilbrunnen (containing alkaline salts and very rich in carbonate of magnesia), and Tönnissteiner Stahlbrunnen.[3]

Lamscheider mineral spring[4] (alkaline salts).

Augustaquelle, Victoriaquelle, Römerquelle, fresh examination of the Kränchen, Fürstenbrunnen, Kesselbrunnen and the new Badequelle at Ems.[5]

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[1] A. Speyer, Arolsen, 1865.

[2] C. W. Kreidel, Wiesbaden, 1866. [3] *Ibid.* 1869. [4] *Ibid.* 1869.

Stahlbrunnen at Homburg, v. d. H.[6]

Carlsquelle at Bad Helmstedt[7] (chalybeate spring).

Deutsch-Kreutzer Sauerbrunnen at Oedenburg[8] (alkaline salts).

New Selser springs at Grosskarben[9] (earthy salts).

Grindbrunnen at Frankfort-on-the-Maine[10] (containing alkaline sulphides).

Mineral spring at Birresborn[11] (alkaline salts).

Mineral spring at Neudorf in Bohemia[12] (alkaline and iron salts).

Thermal spring at Assmannshausen[13] (alkaline salts, rich in lithia).

Mineral spring at Biskirchen[14] (alkaline salts).

Wappenquelle at Ems[15] (alkaline thermal spring).

Thermal brine spring at Werne.[16]

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[5] C. W. KREIDEL, Wiesbaden, 1865, 1869, 1870, 1872. [6] *Ibid.* 1872.
[7] *Ibid.* 1873. [8] *Ibid.* 1874. [9] *Ibid.* 1874.
[10] C. NAUMANN, Frankfort-on-the-Maine, 1874.
[11] C. W. KREIDEL, Wiesbaden, 1876. [12] *Ibid.* 1876. [13] *Ibid.* 1876.
[14] *Ibid.* 1876. [15] *Ibid.* 1876. [16] *Ibid.* 1877.

II. ANALYSIS OF SOME TECHNICAL PRODUCTS AND MINERALS, WITH PROCESSES FOR ESTIMATING THEIR COMMERCIAL VALUE.

1. Determination of Free Acid (Acidimetry).

A. Estimation by Specific Gravity.

§ 214.

Tables have been drawn up, based on the results of exact experiments, and expressing the relation between the specific gravity of the aqueous solution of an acid, and the amount of real acid contained in it; so that to know the amount of real acid contained in an aqueous solution of an acid, it is, in many cases, merely necessary to determine its specific gravity. Of course the acids must be free from, or at least nearly free from, admixtures with other soluble substances; and, as most common acids are volatile (sulphuric acid, hydrochloric acid, nitric acid, acetic acid), any non-volatile admixture may be readily detected by evaporating a sample of the acid in a small platinum or porcelain dish.

The determination of the specific gravity is effected either by comparing the weights of equal volumes of water and acid* (p. 149 or 150), or by means of a good hydrometer. Care must be taken, of course, that the estimations are made at the temperature to which the Tables refer.

The Tables on pages 181–187, give the relations between the specific gravity and the strength for sulphuric acid, hydrochloric acid, nitric acid, phosphoric acid, acetic acid, tartaric acid, and citric acid.

In all cases in which the determination of the specific gravity fails to decide as to the amount of acid in an aqueous solution, or where great accuracy is required, one of the following methods is employed, more commonly the first.

B. Estimation by Saturation of the Acid with an Alkaline Liquid of known strength.†

§ 215.

This method requires:—

α. A dilute acid of known strength.
β. An alkaline liquid of known strength.

aa. Preparation of the Solutions.

1. The *acid* is diluted so as to contain in 1000 c. c. at 17°·5 the exact equivalent number (H=1) of grams of the acid, accordingly, 40 grams

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* Zeitschr. f. Analyt. Chem. 9, 233, and 17, 344.

† According to Nicholson and Price (Chem. Gaz. 1856, p. 30) the common method of acidimetry is not suited for determining free acetic acid, on account of the alkaline reaction of neutral acetate of soda; Otto, however, (Anal. d. Chem. u. Pharm. 102, 69) has clearly demonstrated that the error arising from this is so inconsiderable that it may safely be disregarded.

Table I. A.

Showing the percentages of hydrated and anhydrous acid corresponding with various specific gravities of aqueous *Sulphuric Acid* by Bineau; calculated for 15° C., by Otto.

Specific gravity.	Percentage of hydrated acid.	Percentage of anhydrous acid.	Specific gravity.	Percentage of hydrated acid.	Percentage of anhydrous acid.
1·8426	100	81·63	1·398	50	40·81
1·842	99	80·81	1·3886	49	40·00
1·8406	98	80·00	1·379	48	39·18
1·840	97	79·18	1·370	47	38·36
1·8384	96	78·36	1·361	46	37·55
1·8376	95	77·55	1·351	45	36·73
1·8356	94	76·73	1·342	44	35·82
1·834	93	75·91	1·333	43	35·10
1·831	92	75·10	1·324	42	34·28
1·827	91	74·28	1·315	41	33·47
1·822	90	73·47	1·306	40	32·65
1·816	89	72·65	1·297	39	31·83
1·809	88	71·83	1·2896	38	31·02
1·802	87	71·02	1·281	37	30·20
1·794	86	70·10	1·272	36	29·38
1·786	85	69·38	1·264	35	28·57
1·777	84	68·57	1·256	34	27·75
1·767	83	67·75	1·2476	33	26·94
1·756	82	66·94	1·239	32	26·12
1·745	81	66·12	1·231	31	25·30
1·734	80	65·30	1·223	30	24·49
1·722	79	64·48	1·215	29	23·67
1·710	78	63·67	1·2066	28	22·85
1·698	77	62·85	1·198	27	22·03
1·686	76	62·04	1·190	26	21·22
1·675	75	61·22	1·182	25	20·40
1·663	74	60·40	1·174	24	19·58
1·651	73	59·59	1·167	23	18·77
1·639	72	58·77	1·159	22	17·95
1·637	71	57·95	1·1516	21	17·14
1·615	70	57·14	1·144	20	16·32
1·604	69	56·32	1·136	19	15·51
1·592	68	55·59	1·129	18	14·69
1·580	67	54·69	1·121	17	13·87
1·568	66	53·87	1·1136	16	13·06
1·557	65	53·05	1·106	15	12·24
1·545	64	52·24	1·098	14	11·42
1·534	63	51·42	1·091	13	10·61
1·523	62	50·61	1·083	12	9·79
1·512	61	49·79	1·0756	11	8·98
1·501	60	48·98	1·068	10	8·16
1·490	59	48·16	1·061	9	7·34
1·480	58	47·34	1·0536	8	6·53
1·469	57	46·53	1·0464	7	5·71
1·4586	56	45·71	1·039	6	4·89
1·448	55	44·89	1·032	5	4·08
1·438	54	44·07	1·0256	4	3·26
1·428	53	43·26	1·019	3	2·445
1·418	52	42·45	1·013	2	1·63
1·408	51	41·63	1·0064	1	0·816

Table I. B.

Showing the amount of acid in mixtures of *Sulphuric Acid* and Water at each degree Baumé from 0 to 66, with the corresponding specific gravities, at 15° C., by J. Kolb.*

Degree Baumé.	Specific gravity.	Anhydrous sulphuric acid.	HO,SO_3	Degree Baumé.	Specific gravity.	Anhydrous sulphuric acid.	HO,SO_3
0	1·000	0·7	0·9	34	1·308	32·8	40·2
1	1·007	1·5	1·9	35	1·320	33·9	41·6
2	1·014	2·3	2·8	36	1·332	35·1	43·0
3	1·022	3·1	3·8	37	1·345	36·2	44·4
4	1·029	3·9	4·8	38	1·357	37·2	45·5
5	1·037	4·7	5·8	39	1·370	38·3	46·9
6	1·045	5·6	6·8	40	1·383	39·5	48·3
7	1·052	6·4	7·8	41	1·397	40·7	49·8
8	1·060	7·2	8·8	42	1·410	41·8	51·2
9	1·067	8·0	9·8	43	1·424	42·9	52·8
10	1·075	8·8	10·8	44	1·438	44·1	54·0
11	1·083	9·7	11·9	45	1·453	45·2	55·4
12	1·091	10·6	13·0	46	1·468	46·4	56·9
13	1·100	11·5	14·1	47	1·483	47·6	58·3
14	1·108	12·4	15·2	48	1·498	48·7	59·6
15	1·116	13·2	16·2	49	1·514	49·8	61·0
16	1·125	14·1	17·3	50	1·530	51·0	62·5
17	1·134	15·1	18·5	51	1·540	52·2	64·0
18	1·142	16·0	19·6	52	1·563	53·5	65·5
19	1·152	17·0	20·8	53	1·580	54·9	67·0
20	1·162	18·0	22·2	54	1·597	56·0	68·6
21	1·171	19·0	23·3	55	1·615	57·1	70·0
22	1·180	20·0	24·5	56	1·634	58·4	71·6
23	1·190	21·1	25·8	57	1·652	59·7	73·2
24	1·200	22·1	27·1	58	1·671	61·0	74·7
25	1·210	23·2	28·4	59	1·691	62·4	76·4
26	1·220	24·2	29·6	60	1·711	63·8	78·1
27	1·231	25·3	31·0	61	1·732	65·2	79·9
28	1·241	26·3	32·2	62	1·753	66·7	81·7
29	1·252	27·3	33·4	63	1·774	68·7	84·1
30	1·263	28·3	34·7	64	1·796	70·6	86·5
31	1·274	29·4	36·0	65	1·819	73·2	89·7
32	1·285	30·5	37·4	66	1·842	81·6	100·0
33	1·297	31·7	38·8				

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* Polytechn. Centralbl. 1873, 826. Dingler's polyt. Journ. 209, 268. Zeitschr. f. anal. Chem. 12, 333. Kolb's results agree with Bineau's (Table I. A) very closely, although not absolutely. With reference to Baumé's degrees it should be observed that the zero is determined in pure water at 15° and the degree 66° B. in pure hydrated sulphuric acid of specific gravity 1·842.

Table II. A.

Showing the percentages of Anhydrous Acid corresponding with various specific gravities of Aqueous *Hydrochloric Acid*, by Ure. Temperature 15° C.

Specific gravity.	Percentage of hydrochloric acid gas.	Specific gravity.	Percentage of hydrochloric acid gas.
1·2000	40·777	1·1000	20·388
1·1982	40·369	1·0980	19·980
1·1964	39·961	1·0960	19·572
1·1946	39·554	1·0939	19·165
1·1928	39·146	1·0919	18·757
1·1910	38·738	1·0899	18·349
1·1893	38·330	1·0879	17·941
1·1875	37·923	1·0859	17·534
1·1857	37·516	1·0838	17·126
1·1846	37·108	1·0818	16·718
1·1822	36·700	1·0798	16·310
1·1802	36·292	1·0778	15·902
1·1782	35·884	1·0758	15·494
1·1762	35·476	1·0738	15·087
1·1741	35·068	1·0718	14·679
1·1721	34·660	1·0697	14·271
1·1701	34·252	1·0677	13·863
1·1681	33·845	1·0657	13·456
1·1661	33·437	1·0637	13·049
1·1641	33·029	1·0617	12·641
1·1620	32·621	1·0597	12·233
1·1599	32·213	1·0577	11·825
1·1578	31·805	1·0557	11·418
1·1557	31·398	1·0537	11·010
1·1537	30·990	1·0517	10·602
1·1515	30·582	1·0497	10·194
1·1494	30·174	1·0477	9·786
1·1473	29·767	1·0457	9·379
1·1452	29·359	1·0437	8·971
1·1431	28·951	1·0417	8·563
1·1410	28·544	1·0397	8·155
1·1389	28·136	1·0377	7·747
1·1369	27·728	1·0357	7·340
1·1349	27·321	1·0337	6·932
1·1328	26·913	1·0318	6·524
1·1308	26·505	1·0298	6·116
1·1287	26·098	1·0279	5·709
1·1267	25·690	1·0259	5·301
1·1247	25·282	1·0239	4·893
1·1226	24·874	1·0220	4·486
1·1206	24·466	1·0200	4·078
1·1185	24·058	1·0180	3·670
1·1164	23·650	1·0160	3·262
1·1143	23·242	1·0140	2·854
1·1123	22·834	1·0120	2·447
1·1102	22·426	1·0100	2·039
1·1082	22·019	1·0080	1·631
1·1061	21·611	1·0060	1·124
1·1041	21·203	1·0040	0·816
1·1020	20.796	1·0020	0·408

Table II. B.

Showing the amount of Acid in aqueous *Hydrochloric Acid* at each degree Baumé, from 0 to 25·5, with the corresponding specific gravity at 15° C. by J. Kolb.*

Degree Baumé.	Specific gravity.	100 parts contain:		Degree Baumé.	Specific gravity.	100 parts contain:	
		Hydrochloric acid gas at 0° C.	Hydrochloric acid gas at 15° C.			Hydrochloric acid gas at 0° C.	Hydrochloric acid gas at 15° C.
0	1·000	0·0	0·1	17	1·134	25·2	26·6
1	1·007	1·4	1·5	18	1·143	27·0	28·4
2	1·014	2·7	2·9	19	1·152	28·7	30·2
3	1·022	4·2	4·5	19·5	1·157	29·7	31·2
4	1·029	5·5	5·8	20	1·161	30·4	32·0
5	1·036	6·9	7·3	20·5	1·166	31·4	33·0
6	1·044	8·4	8·9	21	1·171	32·3	33·9
7	1·052	9·9	10·4	21·5	1·175	33·0	34·7
8	1·060	11·4	12·0	22	1·180	34·1	35·7
9	1·067	12·7	13·4	22·5	1·185	35·1	36·8
10	1·075	14·2	15·0	23	1·190	36·1	37·9
11	1·083	15·7	16·5	23·5	1·195	37·1	39·0
12	1·091	17·2	18·1	24	1·199	38·0	39·8
13	1·100	18·9	19·9	24·5	1·205	39·1	41·2
14	1·108	20·4	21·5	25	1·210	40·2	42·4
15	1·116	21·9	23·1	25·5	1·212	41·7	42·9
16	1·125	23·6	24·8				

Table III.

Showing the percentages of Anhydrous Acid corresponding with various specific gravities of Aqueous *Phosphoric Acid*, by J. Watts.†

Sp. gr. at 15·°5 C.	Percentage of PO_5.	Sp. gr. at 15·°5 C.	Percentage of PO_5.	Sp. gr. at 15·°5 C.	Percentage of PO_5.
1·508	49·60	1·328	36·15	1·144	17·89
1·492	48·41	1·315	34·82	1·136	16·95
1·476	47·10	1·302	33·49	1·124	15·64
1·464	45·63	1·293	32·71	1·113	14·33
1·453	45·38	1·285	31·94	1·109	13·25
1·442	44·13	1·276	31·03	1·095	12·18
1·434	43·95	1·268	30·13	1·081	10·44
1·426	43·28	1·257	29·16	1·073	9·53
1·418	42·61	1·247	28·24	1·066	8·62
1·408	41·60	1·236	27·30	1·056	7·39
1·392	40·86	1·226	26·36	1·047	6·17
1·384	40·12	1·211	24·79	1·031	4·15
1·376	39·66	1·197	23·23	1·022	3·03
1·369	39·21	1·185	22·07	1·014	1·91
1·356	38·00	1·173	20·91	1·006	0·79
1·347	37·37	1·162	19·73		
1·339	36·74	1·153	18·81		

* Compt. rend. 74, 337. Zeitsch f. anal. Chem. 11, 339.

† Journ. Chem. Soc. 19, 499. Journ. f. prakt. Chem. 101, 59. Zeitschr. anal. Chem. 7, 357.

Table IV.

Showing the percentages corresponding with various specific gravities of aqueous *Nitric Acid*, Hydrated, and Anhydrous Acid, by J. Kolb.*

100 parts contain :		Specific gravity.		100 parts contain :		Specific gravity.	
HO,NO_5.	NO_5.	at 0° C.	at 15° C.	HO,NO_5.	NO_5.	at 0° C.	at 15° C.
100·00	85·71	1·559	1·530	58·88	50·47	1·387	1·368
99·84	85·57	1·559	1·530	58·00	49·71	1·382	1·363
99·72	85·47	1·558	1·530	57·00	48·86	1·376	1·358
99·52	85·30	1·557	1·529	56·10	48·08	1·371	1·353
97·89	83·90	1·551	1·523	55·00	47·14	1·365	1·346
97·00	83·14	1·548	1·520	54·00	46·29	1·359	1·341
96·00	82·28	1·544	1·516	53·81	46·12	1·358	1·339
95·27	81·66	1·542	1·514	53·00	45·40	1·353	1·335
94·00	80·57	1·537	1·509	52·33	44·85	1·349	1·331
93·01	79·72	1·533	1·506	50·99	43·70	1·341	1·323
92·00	78·85	1·529	1·503	49·97	42·83	1·334	1·317
91·00	78·00	1·526	1·499	49·00	42·00	1·328	1·312
90·00	77·15	1·522	1·495	48·00	41·14	1·321	1·304
89·56	76·77	1·521	1·494	47·18	40·44	1·315	1·298
88·00	75·43	1·514	1·488	46·64	39·97	1·312	1·295
87·45	74·95	1·513	1·486	45·00	38·57	1·300	1·284
86·17	73·86	1·507	1·482	43·53	37·31	1·291	1·274
85·00	72·86	1·503	1·478	42·00	36·00	1·280	1·264
84·00	72·00	1·499	1·474	41·00	35·14	1·274	1·257
83·00	71·14	1·495	1·470	40·00	34·28	1·267	1·251
82·00	70·28	1·492	1·467	39·00	33·43	1·260	1·244
80·96	69·39	1·488	1·463	37·95	32·53	1·253	1·237
80·00	68·57	1·484	1·460	36·00	30·86	1·240	1·225
79·00	67·71	1·481	1·456	35·00	29·29	1·234	1·218
77·66	66·56	1·476	1·451	33·86	29·02	1·226	1·211
76·00	65·14	1·469	1·445	32·00	27·43	1·214	1·198
75·00	64·28	1·465	1·442	31·00	26·57	1·207	1·192
74·01	63·44	1·462	1·438	30·00	25·71	1·200	1·185
73·00	62·57	1·457	1·435	29·00	24·85	1·194	1·179
72·39	62·05	1·455	1·432	28·00	24·00	1·187	1·172
71·24	61·06	1·450	1·429	27·00	23·14	1·180	1·166
69·96	60·00	1·444	1·423	25·71	22·04	1·171	1·157
69·20	59·31	1·441	1·419	23·00	19·71	1·153	1·138
68·00	58·29	1·435	1·414	20·00	17·14	1·132	1·120
67·00	57·43	1·430	1·410	17·47	14·97	1·115	1·105
66·00	56·57	1·425	1·405	15·00	12·85	1·099	1·089
65·07	55·77	1·420	1·400	13·00	11·14	1·085	1·077
64·00	54·85	1·415	1·395	11·41	9·77	1·075	1·067
63·59	54·50	1·413	1·393	7·22	6·62	1·050	1·045
62·00	53·14	1·404	1·386	4·00	3·42	1·026	1·022
61·21	52·46	1·400	1·381	2·00	1·71	1·013	1·010
60·00	51·43	1·393	1·374	0·00	0·00	1·000	0·999
59·59	51·08	1·391	1·372				

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* Ann. chim. phys. [4] 10, 140. Zeitsch. f. anal. Chem. 5, 449.

Note.—There are several discrepancies in this table; the ratio between $HO,NO_5 = 63$, and $NO_5 = 54$, being 7 : 6. The number NO_5 corresponding with 35·00, HO,NO_5 should be 30, whereas it is given as 29·29 in the table; again, 7·22 HO,NO_5 corresponds with 6·18 NO_5 instead of 6·62.—Editor.

Table V.

Showing the percentages of Hydrated *Acetic Acid* corresponding with various specific gravities of Aqueous Acetic Acid, by A. C. OUDEMANS.*

Percentage of hydrated acetic acid.	Specific gravity at 15° C.	Specific gravity at 20° C.
0	0·9992	0·9983
1	1·0007	0·9997
2	1·0022	1·0012
3	1·0037	1·0026
4	1·0052	1·0041
5	1·0067	1·0055
6	1·0083	1·0069
7	1·0098	1·0084
8	1·0113	1·0098
9	1·0127	1·0112
10	1·0142	1·0126
11	1·0157	1·0140
12	1·0171	1·0154
13	1·0185	1·0168
14	1·0200	1·0181
15	1·0214	1·0195
16	1·0228	1·0208
17	1·0242	1·0222
18	1·0256	1·0235
19	1·0270	1·0248
20	1·0284	1·0261
21	1·0298	1·0274
22	1·0311	1·0287
23	1·0324	1·0299
24	1·0337	1·0312
25	1·0350	1·0324
26	1·0363	1·0336
27	1·0375	1·0348
28	1·0388	1·0360
29	1·0400	1·0372
30	1·0412	1·0383
31	1·0424	1·0394
32	1·0436	1·0405
33	1·0447	1·0416
34	1·0459	1·0426
35	1·0470	1·0437
36	1·0481	1·0448
37	1·0492	1·0458
38	1·0502	1·0468
39	1·0513	1·0478
40	1·0523	1·0488
41	1·0533	1·0498
42	1·0543	1·0507
43	1·0552	1·0516
44	1·0562	1·0525
45	1·0571	1·0534
46	1·0580	1·0543
47	1·0589	1·0551
48	1·0598	1·0559
49	1·0607	1·0567
50	1·0615	1·0575
51	1·0623	1·0583
52	1·0631	1·0590
53	1·0638	1·0597
54	1·0646	1·0604
55	1·0653	1·0611
56	1·0660	1·0618
57	1·0666	1·0624
58	1·0673	1·0630
59	1·0679	1·0636
60	1·0685	1·0642
61	1·0691	1·0648
62	1·0697	1·0653
63	1·0702	1·0658
64	1·0707	1·0663
65	1·0712	1·0667
66	1·0717	1·0671
67	1·0721	1·0675
68	1·0725	1·0679
69	1·0729	1·0683
70	1·0733	1·0686
71	1·0737	1·0689
72	1·0740	1·0691
73	1·0742	1·0693
74	1·0744	1·0695
75	1·0746	1·0697
76	1·0747	1·0699
77	1·0748	1·0700
78	1·0748	1·0700
79	1·0748	1·0700
80	1·0748	1·0699
81	1·0747	1·0698
82	1·0746	1·0696
83	1·0744	1·0694
84	1·0742	1·0691
85	1·0739	1·0688
86	1·0736	1·0684
87	1·0731	1·0679
88	1·0726	1·0674
89	1·0720	1·0668
90	1·0713	1·0660
91	1·0705	1·0652
92	1·0696	1·0643
93	1·0686	1·0632
94	1·0674	1·0620
95	1·0660	1·0606
96	1·0644	1·0589
97	1·0625	1·0570
98	1·0604	1·0549
99	1·0580	1·0525
100	1·0553	1·0497

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* "The Specific Gravity of Acetic acid and Mixtures of the Acid with Water." Max Cohen and Son. Bonn: 1866. Zeitsch. f. anal. Chem. 5, 453.

Table VI.

Showing the percentages of crystallized *Tartaric* and *Citric Acids* corresponding with various specific gravities of aqueous solutions of the acids, by Gerlach.*

Percentage by weight in the solution.	Crystallized tartaric acid, specific gravity at 15° C.	Crystallized citric acid, specific gravity at 15° C.	Percentage by weight in the solution.	Crystallized tartaric acid, specific gravity at 15° C.	Crystallized citric acid, specific gravity at 15° C.
1	1·0045	1·0037	34	1·1726	1·1422
2	1·0090	1·0074	35	1·1781	1·1467
3	1·0136	1·0111	36	1·1840	1·1515
4	1·0179	1·0149	37	1·1900	1·1564
5	1·0224	1·0186	38	1·1959	1·1612
6	1·0273	1·0227	39	1·2019	1·1661
7	1·0322	1·0268	40	1·2078	1·1709
8	1·0371	1·0309	41	1·2138	1·1756
9	1·0420	1·0350	42	1·2198	1·1814
10	1·0469	1·0392	43	1·2259	1·1851
11	1·0517	1·0431	44	1·2317	1·1899
12	1·0565	1·0470	45	1·2377	1·1947
13	1·0613	1·0509	46	1·2441	1·1998
14	1·0661	1·0549	47	1·2504	1·2050
15	1·0709	1·0588	48	1·2568	1·2103
16	1·0761	1·0632	49	1·2632	1·2153
17	1·0813	1·0675	50	1·2696	1·2204
18	1·0865	1·0718	51	1·2762	1·2257
19	1·0917	1·0762	52	1·2828	1·2307
20	1·0969	1·0805	53	1·2894	1·2359
21	1·1020	1·0848	54	1·2961	1·2410
22	1·1072	1·0889	55	1·3027	1·2462
23	1·1124	1·0930	56	1·3093	1·2514
24	1·1175	1·0972	57	1·3159	1·2572
25	1·1227	1·1014	58		1·2627
26	1·1282	1·1060	59		1·2683
27	1·1338	1·1106	60		1·2738
28	1·1393	1·1152	61		1·2794
29	1·1449	1·1198	62		1·2849
30	1·1505	1·1244	63		1·2904
31	1·1560	1·1288	64		1·2960
32	1·1615	1·1333	65		1·3015
33	1·1670	1·1378	66		1·3071

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* Zeitsch. f. anal. Chem. 8, 295.

sulphuric acid, 36·46 hydrochloric acid, 36 oxalic acid, &c. Acids of this strength are called *normal acids;* equal volumes of them have the same power of saturating alkalies. Normal sulphuric acid or normal hydrochloric acid is generally employed, or else normal oxalic acid, as recommended by MOHR.

2. For the *alkaline solution*, a solution of caustic soda is used of such strength that one volume is sufficient to neutralize exactly one volume of the normal acid, so that on mixing the two the last drop of the soda solution imparts a blue colour to the acid solution which has been previously faintly reddened by means of litmus. A soda solution of this strength is called *normal soda solution;* 1000 c. c. of it saturate one equivalent of any monobasic acid ($H = 1$), expressed in grams.

Various methods may be employed for preparing the normal acids; of these the most generally used (*a*), in which pure anhydrous carbonate of soda serves as the standard, is available for all acids, whilst the others (*b*) can only be employed for the valuation of individual normal acids. The method of preparing the normal soda solution will be described under (*a*) and also under (*b*).

a. GENERAL METHODS (BY NEUTRALIZATION).

1. Requisites.

The following are required:—

α. Pure carbonate of soda to serve as a standard. This is most easily prepared from the purest commercial bicarbonate of soda; it should be powdered, placed in a funnel which has a small filter in it, pressed down firm, and the surface rendered even; several layers of filter paper are then laid on it, and small quantities of cold distilled water poured on in succession. This method of washing is continued until the liquid which runs through is quite free from sulphuric acid and from chlorine. The washed salt is then dried, and heated—preferably in a platinum basin—until the bicarbonate of soda is converted into the anhydrous monocarbonate; after which powdered and preserved for use. Before weighing it out, the requisite quantity is heated moderately for a long time in a platinum crucible, and is then transferred while still hot to a warm dry tube, which must be closed tightly and kept under a desiccator.

β. The Alkali Solution.—Caustic soda solution is used for this purpose; it should have a sp. gr. of from 1·046 to 1·048 as determined by the hydrometer, and will contain somewhat more than 1 equiv. of soda in the litre, namely, about 32 to 34 grams. The use of the hydrometer can be avoided if a soda solution of convenient strength is to hand; in this case a rough determination is made, and it is diluted so that 20 c. c. of the normal acid is saturated by about 19 to 19·5 c. c. of the soda solution. If it is desired to remove the carbonic acid from a concentrated solution of caustic soda, containing some carbonate, it should first be diluted and heated to boiling; some milk of lime is then added, the whole boiled, and when cooled somewhat, the mixture is placed in a flask and allowed to settle. The flask should be closed with a perforated cork fitted with a bulb tube containing soda-lime (this vol. p. 191). When quite clear, the solution is drawn off into another flask by means of a syphon.

γ. Dilute Acid which contains somewhat more than 1 equiv. of the acid (H = 1) in grams per litre; for example, dilute sulphuric acid containing 41 to 42 grams of the anhydrous acid per litre, hydrochloric acid containing about 37 to 39 grams of hydrogen chloride per litre, &c. It is all sufficient to determine the strength of the respective acids by means of the hydrometer; and the following may be taken as the limits of sp. gr. at 15°:—

Dilute sulphuric acid	1·032 to 1·033
„ hydrochloric acid . . .	1·018 to 1·019
„ nitric acid	1·037 to 1·038

δ. *Tincture of Litmus.*—As the tincture of litmus is often so alkaline that a notable amount of acid is required to redden it, the excess of alkali must, if necessary, be neutralized; the tincture so prepared gives upon dilution with water a violet-coloured fluid, to which a trace of acid imparts a red, and the least quantity of alkali a blue tint (§ 65, 2).

Special kinds of tincture of litmus and other indicators used to ascertain when solutions are neutral are treated of hereafter (§ 215, 6).

Having prepared the requisites, we proceed:

2. To determine accurately the amount of acid in the dilute acid.
3. To dilute the acid to normal strength.
4. To dilute the soda solution to normal strength.

2. Accurate Determination of the Acid.

a. A burette with pinchcock is filled to the zero point with the dilute acid (1. γ.), and a second burette with the alkaline solution (1. β.). 20 c. c. of the acid is then run out into a beaker containing about 100 c. c. of water, and it is coloured slightly red with tincture of litmus; the soda solution is then run in until the liquid becomes just distinctly blue. If this point is not hit exactly, some more acid must be added, and then soda solution, until the desired accuracy is attained. In this way, the relation of the soda solution to the acid is ascertained. Suppose, for example, that 20 c. c. of the acid has taken 19·5 c. c. of soda solution to neutralize it.

The two burettes are now refilled to the zero point with the acid and alkali respectively.

β. Two portions of the pure anhydrous carbonate of soda, from 1·0 to 1·5 gram each, are now weighed out; these are introduced into two flasks of 300 c. c. capacity, and each is dissolved in 100 to 150 c. c. of water.

γ. One of the solutions of carbonate of soda thus prepared is warmed and coloured *pale* blue with tincture of litmus; the acid from the burette is run in in small quantities at a time with constant agitation until the liquid is of a reddish violet colour, and it is then heated and kept gently boiling for a time. In this way, the free carbonic acid is expelled, and the liquid gradually becomes blue again. More acid is now run in until the colour becomes yellowish-red, the liquid is boiled for a few minutes, and then soda solution is run in carefully until the colour is distinctly blue. If this point is not hit exactly, some more acid must be added, and then soda solution until the right tint is attained. After the lapse of a few minutes, the level of the solutions in the burettes is read off, and the excess of dilute acid employed above that necessary to neutralize the carbonate of soda is reckoned from the amount of soda solution used, according to the proportion found in 2 *a*. This excess subtracted from the total quantity of acid gives the acid used in saturating the weighed quantity of carbonate of soda, and consequently the exact amount of real acid contained in the dilute acid; 1 equiv. of carbonate of soda, or 53·04 grams corresponding with 1 equiv. of the acid, that is, with 40 grams of sulphuric acid, 36·46 of hydrochloric acid, or 54·04 of nitric acid.

An example will illustrate this. Weight of carbonate of soda, 1·2 gram. Total hydrochloric acid used 22 c. c., and 1·2 c. c. of soda solution. 20 of the dilute acid corresponds with 19·5 of the soda solution.

As 19·5 c. c. of the soda solution corresponds with 20 c. c. of the dilute hydrochloric acid, the 1·2 c. c. will correspond with 1·23 of the acid. Therefore the acid required to saturate the carbonate of soda was 22−1·23 = 20·77 c. c., and this contains hydrogen chloride equivalent to 1·2 grams carbonate of soda, which on calculation from the proportion, 53·04 : 36·46 :: 1·2 : x, gives 0·80647 grams HCl. And as 20·77 c. c. of the dilute acid contains 0·80647 grams HCl, 1000 c. c. will contain 38·828 grams.

The second portion of carbonate of soda is treated in exactly the same way, and a comparison of the two results made to see if they are alike or nearly alike. For this purpose it is most convenient to calculate the results of both experiments to 1 gram of carbonate of soda. A closer agreement than 0·1 in the amount of acid in 1000 c. c. cannot be expected, as under the conditions of the experiment given in the example this corresponds with 0·05 c. c. of the acid employed. If the first experiment, for instance, gave 38·828 grams hydrogen chloride in 1000 c. c. and the second 38·928, there would be no need to make a third determination. If the difference is considerably greater, however—that is, much more than 0·05 c. c. of the dilute acid per gram of carbonate of soda—a fresh portion of carbonate of soda must be weighed out and a third determination made.

3. Preparation of Normal Acid.

When the amount of anhydrous acid in the dilute acid has been determined as described in 2, it has to be diluted so as to prepare normal acid, that is, so that 1000 c. c. of the acid measured at 17·5° shall contain the equivalent of the respective acid in grams (H = 1). Suppose—as in the above example—that 1000 c. c. of the hydrochloric acid are found to contain by the first experiment 38·828 grams, by the second 38·928, mean 38·878 grams of hydrogen chloride. It will then be necessary from the equation:

$$36{\cdot}46 : 1000 :: 38{\cdot}878 : x \qquad \therefore x = 1066{\cdot}3$$

to add distilled water so as to make up each 1000 c. c. of this dilute acid to 1066·33 c. c. This can be done accurately and conveniently as follows:—A measuring flask of 1 litre capacity is filled to the mark with the acid at a temperature of 17·5°, and this is then carefully poured into a somewhat larger dry bottle (intended for storing the normal acid), 66·3 c. c. of water are measured out in a burette or pipette, and transferred to the measuring flask which contained the acid, and after being well shaken about in the flask, the water is added to the solution in the bottle. This is then well shaken, about half of the liquid poured back again into the measuring flask, shaken about in the latter, and then transferred again to the bottle. Finally the whole is shaken and kept for use. If the liquid only partly fills the bottle, water will evaporate, and condense on the sides in the upper part of the vessel; it is necessary, therefore, to shake the bottle each time before its contents are used; otherwise the portion poured out first would contain more water than the remaining fluid, and consequently this would increase gradually in strength.*

4. Preparation of Normal Soda Solution.

By *normal soda solution* is meant a soda solution of which 1 volume exactly neutralizes 1 volume of normal acid, so that on mixing the two the last drop of soda solution renders distinctly blue the normal acid coloured slightly red by litmns. 1000 c. c. of such a soda solution measured at 17·5 will saturate 1 equiv. of each monobasic acid ($H = 1$) expressed in grams.

Although the proportion in which it is necessary to dilute the soda solution may be determined from the relation already determined (2 α) between the original acid solution (2 γ, the strength of which is now accurately determined) and the soda solution (2 β), it is simpler to ascertain experimentally the relation between the soda solution and the recently prepared normal acid, that is, how much of the soda solution must be added to 20 or 30 c. c. of the normal acid diluted with 100 c. c. distilled water and coloured pale red with litmus, in order to render it distinctly blue. Suppose 27·4 c. c. of the soda are required to neutralize 30 c. c. of the normal acid, then to 27·4 c. c. of the soda, 30–27·4 = 2·6 c. c. of distilled water must be added to render it normal, or 94·9 c. c. to 1000 c. c. of the soda solution. The best way of doing this has been already described in the preparation of the normal acid (in 3).

The bottle in which the normal soda solution is to be kept should be closed, as Mohr recommends, with a cork, into which is fitted a small bulb tube of the form of a chloride of calcium tube. This is filled with soda lime, and furnished with a thin open tube at the upper end (fig. 93).

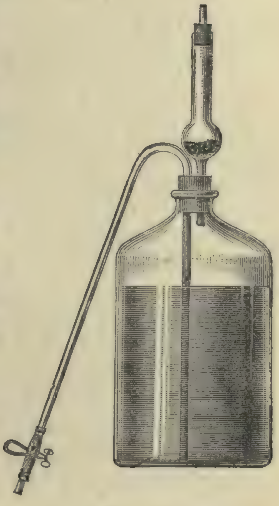

Fig. 93.

Besides this normal solution, it is advisable to have others respectively five times and ten times as dilute. The dilution is best effected —for example as regards the more dilute—by introducing into a measuring flask marked accurately at 500 c. c., 50 c. c. of the normal soda solution by means of a graduated pipette or burette, filling the flask accurately to the mark with water and shaking well.

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* This rule of course applies to standard solutions generally.

b. SPECIAL METHODS FOR PREPARING NORMAL ACID AND NORMAL ALKALI SOLUTIONS.

1. Preparation of Normal Sulphuric Acid.

For this purpose the dilute sulphuric acid of sp. gr. 1·032 to 1·033 (this vol. p. 189) is used. Two quantities of 20 c. c. each are accurately measured out (best by means of a burette), and the sulphuric acid in them determined by precipitation with chloride of barium (§ 132, I. 1.). If the results of the two determinations agree well, the mean is taken and the sulphuric acid is diluted so that 1000 c. c. contain exactly 40 grams of anhydrous sulphuric acid, SO_3. For example, if 20 c. c. of the acid contain 0·840 gram SO_3, 1000 c. c. will contain 42 grams. From the proportion

$$40 : 1000 : 42 : x$$

we find that water must be added to 1000 c. c. of our acid so as to make it up to 1050 c. c.

The best method of doing this has been already described (this vol. pp. 190, 191).

2. Preparation of Normal Hydrochloric Acid.

The dilute acid of sp. gr. 1·018 to 1·019 is used for this purpose; it should leave no residue when evaporated to dryness in a platinum or porcelain dish. Two quantities of 20 c. c. each are accurately measured out (best by means of a burette), and the hydrochloric acid in them determined; for this purpose they are diluted, some nitric acid added, precipitated with nitrate of silver solution, and the chloride of silver weighed (§ 141, i. *a*). If the two results agree, the mean is taken, and a calculation made as to how much water must be added to 1000 c. c. of the hydrochloric acid so as to give acid of normal strength. For example, if 20 c. c. of the acid contain 0·780 gram HCl, 1000 c. c. will contain 39·0 grams:

$$36{\cdot}46 : 1000 :: 39 : x \qquad \therefore x = 1069{\cdot}7.$$

From this it follows that 69·7 c. c. of water must be added to 1000 c. c. of the acid so as to make it up to 1069·7 c. c. The method of mixing and storing have already been described (this vol. pp. 190, 191).

3. Preparation of Normal Oxalic Acid.

An essential condition is perfectly pure oxalic acid, free from acid oxalate of potash, oxalate of lime, sulphuric acid and sulphates. The method which MOHR recommends for its preparation is given in Vol. I. p. 102. REISCHAUER* who, according to MOHR's paper, did not obtain pure oxalic acid, but one containing a little potash, recommended that it should be made by acting on starch with nitric acid in the laboratory. HABEDANCK† dissolves commercial oxalic acid in the smallest possible quantity of hot absolute alcohol. The solution filtered off from the residue of oxalate of lime and acid oxalate of potassa, after standing for some hours, deposits crystals of oxalic acid (the mother liquor can be used for dissolving a fresh quantity of the commercial acid) which are thoroughly drained and recrystallised from boiling distilled water. F. Stolba* dissolves commercial oxalic acid in boiling hydrochloric acid of 10 to 15 per cent., filters, cools the hot solution quickly with continual stirring, removes the mother liquor from the crystalline powder on a vacuum filter, washes with small quantities of cold water until the drainings contain only a very small quantity of hydrochloric acid, dissolves in boiling water and again allows it to cool with stirring.

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* Ding. polyt. Journ. 167, 47. Zeitsch. f. anal. Chem. 2, 426.

† Zeitsch. anal. Chem. 11, 282.

The method by which crystallised oxalic acid is tested for purity, and properly dried so as to give the formula $HO,C_2O_3 + 2aq.$, and therefore the equivalent 63 is given in § 65, i. It is to be noted that the solution of the crystals must be tested for free sulphuric acid and sulphates by seeing whether it remains clear on the addition of chloride of barium after being acidified with hydrochloric acid.†

The oxalic acid is generally employed in the crystalline state as $HO,C_2O_3 + 2aq.$, but, as O. L. Erdmann has recommended, it may also be converted into the hydrate free from water of crystallisation (HO,C_2O_3) by heating it at 100° until the weight is constant. In the first case 63, and in the latter 45 grams are accurately weighed out, transferred to a litre flask, some water added, and the acid dissolved by shaking; the solution is then diluted at 17·5° to the mark, shaken, and kept where it is not exposed to direct sunlight.‡ Before using, the bottle should be shaken for the reasons previously given.

It should be noted that only concentrated solutions of oxalic acid, such as normal oxalic acid, can be preserved in the manner described, without suffering decomposition; more dilute solutions, on the other hand, such as decinormal acid, undergo change and the oxalic acid is gradually decomposed (G. Bizio §). According to Neubauer,|| the decomposition is accompanied by fungoid growth, but can be entirely prevented if the finished decinormal oxalic acid solution is heated for half-an-hour, in securely closed vessels at 60° to 70° in a water bath.

4. Preparation of Normal Alkali.

It is also necessary to have a normal alkaline solution to use along with the normal acid solutions prepared according to the methods just given. This is made from a solution of soda (free from carbonate) of sp. gr. 1·046 to 1·048. Its relation to the normal acid is determined, and it is diluted so as to accurately correspond with it in the manner described (this vol. p. 191).

II. Verification of the Standard Acid and Alkali.

Although the test-solutions, prepared as directed, must of necessity be correct, if the operations have been carefully performed, it is better to be certain of their accuracy before using them. This is effected in the following manner :—First, a fresh experiment is made to ascertain whether equal volumes of the two liquids when mixed actually neutralise each other. Two portions of carbonate of soda of 1 to 1·5 gram each,

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* Zeitschr. f. anal. Chem. 13, 50.

† O. Binder, *ibid.* 16, 334.

‡ Wittstein, *ibid.* 1 496.

§ *Ibid.* 9, 392.

|| *Ibid.* 9, 392.

chemically pure and completely deprived of all water by gentle ignition, are then weighed out and treated as described, p. 189, γ. Finally, the quantity of carbonate of soda corresponding theoretically with the amount of acid used is calculated thus:

$$1000 : \text{the c.c. of acid used} :: 53{\cdot}04\ (\text{eq. } NaO,CO_2) : x.$$

The result should agree with the known weight of carbonate employed. Differences of 1 to 3 mgrm. are within the allowed limits of error. It is advisable to repeat the experiment with the second quantity of carbonate of soda.

For verifying the normal hydrochloric acid (also the normal nitric acid) pure Iceland spar may be used instead of carbonate of soda. The mineral is powdered, dried at 100°, and two portions of 1 to 1·5 gram each are weighed out. The powder is shaken into a flask, some water added, and the acid is run in from a burette filled to the zero point until complete solution has taken place; this may be aided by *gentle* warming, but a stronger heat must be avoided as yet, as the liquid may contain more than a very slight excess of hydrochloric acid, and in that case it might lose hydrochloric acid if strongly heated. Tincture of litmus is added as soon as dissolution is complete, so that the liquid may be slightly red, and soda solution is run in from a burette filled to the zero point until only a very small excess of acid remains. The solution is now boiled gently for several minutes to expel the carbonic acid, and finally soda is added until the liquor is just blue. The soda is deducted from the acid and the calculation proceeded with as above.

III. Estimation of Free Acid.

a. Ordinary process.

As 1000 c.c. of the normal solution of soda correspond with the equivalent number of grams of each acid, 1000 c.c. of the 5 times more dilute solution with $\frac{1}{5}$ gram-equivalent, and 1000 c.c. of the decinormal solution with $\frac{1}{10}$ gram-eq., there is hardly anything further to be said about the process, the selection of either of these three alkaline liquids depending, of course, entirely on the quantity of acid to be neutralised; the neutralisation of the weighed or measured acid liquid should take about 15 to 30 c.c. Towards the end this must be added very cautiously until the liquid coloured red with tincture of litmus just becomes blue.

In scientific investigations, the author recommends the weighing of indeterminate quantities of the acid liquid, as this can be far more easily done on a chemical balance, and the trifling calculation is but little trouble. Suppose, for instance, that 4·5 grams of a dilute acetic acid had been weighed out, and 25 c.c. normal solution of soda used to neutralise this, the proportion,

$$1000 : 25 :: 60\ (\text{eq. } C_4\,H_4\,O_4) : x \qquad \therefore x = 1{\cdot}5,$$

shows that 1·5 gram of hydrated acetic acid are contained in the weighed quantity of the dilute acid; and another proportion, viz.,

$$4{\cdot}5 : 1{\cdot}5 :: 100 : x \qquad \therefore x = 33{\cdot}33$$

gives the percentage of hydrated acetic acid contained in the liquid analysed. Or the calculation may be made as follows:—

54
64
118

4·5 grams of the acetic acid examined having required 25 c.c. of normal solution of soda for neutralisation, how much would 6 grams (that is, the weight of $\frac{1}{10}$ gram-eq. of hydrated acetic acid) require?

$$4{\cdot}5 : 6 :: 25 : x \qquad \therefore x = 33{\cdot}33$$

It is evident that in this case the number of c.c. found as x expresses the percentage of hydrated acetic acid, since 100 c.c. of normal solution of soda corresponds with $\frac{1}{10}$ gram-eq. of pure hydrated acid, that is, acetic acid of 100 per cent.

In technical analyses, it is more convenient if the number of c.c. or half c.c. of the normal solution of soda used expresses directly the percentage of hydrated or anhydrous acid contained in the liquid examined. For this purpose, the $\frac{1}{10}$ or $\frac{1}{20}$ equivalent number ($H = 1$) of grams of the hydrated or anhydrous acid, are weighed out according as the number of c.c. or half c.c. of normal alkali used is to express the percentage of hydrated or anhydrous acid contained in the liquid analysed.

The following are the quantities for the more common acids :—

	$\frac{1}{10}$ Eq. number of grams.	$\frac{1}{20}$ Eq. number of grams.
Sulphuric acid	4·0	2·00
Hydrated sulphuric acid	4·9	2·45
Nitric acid	5·404	2·702
Hydrated nitric acid	6·304	3·152
Hydrochloric acid	3·646	1·823
Oxalic acid	3·6	1·80
Crystallised oxalic acid	6·3	3·15
Acetic acid	5·1	2·55
Hydrated acetic acid	6·0	3·00
Tartaric acid	6·6	3·30
Hydrated tartaric acid	7·5	3·75

But, as the weighing of definite small quantities would hardly be accurate enough, it is preferable to weigh off half the gram-eq. of the acids (that is, 20 or 24·5 grams of sulphuric acid, according to whether it is intended to find the percentage of anhydrous or of hydrated acid; 18·23 of hydrochloric acid, &c.) in a measuring flask holding 500 c.c., add water cautiously (in the case of concentrated sulphuric acid, the flask must be half full of water before the acid is weighed into it), allow to cool if necessary, fill up with water to the mark, shake, and then remove, by means of the pipette, 100 or 50 c.c., according to whether $\frac{1}{10}$ or $\frac{1}{20}$ gram-eq. of acid is to be used.

b. Deviations from the preceding method.

1. Chemists occasionally prefer using a solution of soda, which is moderately near the correct concentration, straight away, without bringing it to the normal strength, its strength being ascertained by means of a normal acid. This renders a short rule-of-three calculation indispensable. Suppose 18·5 c.c. of solution of soda are found to correspond with 10 c.c. normal sulphuric acid, that is, $\frac{1}{100}$ gram-eq. or 0·4 gram of sulphuric acid, they will correspond equally with $\frac{1}{100}$ gram-eq. of all other acids, accordingly, for instance, with 0·6 gram hydrated acetic

acid. Now, supposing 12 c.c. of the solution of soda to have been used to saturate 10 grams of vinegar, the amount of hydrated acetic acid contained in the latter will be found by the following proportion:—

$$18{\cdot}5 : 12 :: 0{\cdot}6 : x \qquad \therefore x = 0{\cdot}389,$$

and expressed in per-cents.,

$$10 : 0{\cdot}389 :: 100 : x \qquad \therefore x = 3{\cdot}89$$

2. It is often preferable to have the alkali of such a strength that the c.c. or the half c.c. employed to neutralise a round number of grams or c.c. of an aqueous acid may express at once the percentage of real acid. For instance, if 20 c.c. water is added to 1000 c.c. normal soda solution, these 1020 c.c. will saturate 51 (1 eq.) grams of anhydrous acetic acid; 1000 c.c. therefore saturate 50 grams. Hence if 10 grams of vinegar is taken (10 c.c. will do instead, as the sp. gr. of vinegar scarcely differs from that of water), and the diluted solution of soda added to saturation, that is until the liquid coloured with tincture of litmus becomes just blue, the c.c. used, divided by 2, will express the percentage of anhydrous acetic acid in the specimen of vinegar examined.*

3. If the colour of a liquid conceals the change in the dissolved litmus, red litmus or turmeric paper must be used to indicate the point of neutralisation, that is, alkali is added until a strip of test paper dipped in just indicates a feeble alkaline reaction. In this case, more alkali will be employed to blue the litmus than when it is used in solution, and in exact determinations it may be worth while to rectify the error by a correction. This may be done by taking a like quantity of water and adding soda solution, until the liquid just gives a reaction with the test paper in question, as strong as that obtained at the close of the first experiment. The quantity of alkali used must of course be deducted from the quantity employed in the first experiment.

This method is used in testing crude argol for the amount of acid tartrate of potash it contains. If $\frac{1}{10}$ eq. or 18·813 grams is weighed out, the number of c.c. of soda solution used gives at once the percentage of acid tartrate of potash; as this quantity is too large, one-fourth of it can be taken, viz., 4·703 grams, and the number of c.c. of soda solution employed multiplied by 4. One important point in the analysis of crude tartar is that, on account of its high equivalent, a small difference in the amount of soda solution used will seriously affect the result. If 4·703 grams used in one experiment require 21·7 c.c., and in a second experiment 21·6 c.c. of the soda solution, the one gives a percentage of $21{\cdot}7 \times 4 = 86{\cdot}8$, and the other $21{\cdot}6 \times 4 = 86{\cdot}4$.

The argol should be in very fine powder. It is heated and agitated with water, and soda solution is added with prolonged heating until a drop of the liquid gives a brownish spot on a strip of turmeric paper, or a blue spot on a strip of reddened litmus paper. In a second experiment, almost the whole of the soda solution required in the first can be added at once; then, after a sufficiently long heating, more is added, drop by drop, until the final reaction. According to the author's experiments, a trustworthy result cannot be obtained by adding soda solution in excess, heating, adding normal acid, and then lastly normal soda until neutral. This gives, after subtracting the normal acid from the soda solution, too high a number for the soda solution, and thus too high a result, as the colouring matters combine with soda. In accurate analyses the above-mentioned correction must not be omitted. It can easily be understood that this method of analysis of tartars is only admissible if the tartar to be tested contains no other substances with an acid reaction except bitartrate of potassa.*

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* Zeitschr. f. anal. Chem. 1, 253.

4. The titration of free (tribasic) *phosphoric acid* with normal alkali does not succeed, because the so-called neutral soda salt ($2NaO,HO,PO_5$), which has an alkaline reaction, and the acid salt ($NaO,2HO,PO_5$), which has an acid reaction, do not neutralise one another, so that the acid reaction of the one is manifest along with the alkaline reaction of the other. When phosphoric acid is neutralised by soda solution, it will be found that at a certain stage in the operation the liquid turns red litmus paper blue, and reddens blue litmus paper. This point, which was noticed long ago in many urines, was called by BAMBERGER † *amphoter*. Milk shows a similar reaction (SOXHLET ‡). If it is necessary to determine the free phosphoric acid by acidimetry, or to ascertain how much base is required for the formation of the basic salt ($3NaO,PO_5$), the formation of a soluble alkaline phosphate must be prevented, that is to say, the phosphoric acid must be removed from the solution, and, indeed, as a compound of known constitution. MALY § has based on this principle a method of acidimetry, by which phosphoric acid, whether free or combined with alkalies, can be determined with tolerably satisfactory results. The phosphoric acid is precipitated as $3BaO,PO_5$. The method is as follows:—The solution (not too concentrated) of the free phosphoric acid, or the neutral or acid alkali phosphate respectively is measured into a flask, a measured quantity of $\frac{1}{2}$ or $\frac{1}{4}$ normal soda solution is added, more than sufficient to convert all the phosphoric acid into the basic salt; the solution is then coloured with the indicator, an indefinite but sufficient quantity of chloride of barium is added, and it is heated and titrated with $\frac{1}{2}$ or $\frac{1}{4}$ normal acid to acid reaction. The liquid must be kept *hot* during the experiment.

The phosphate of baryta floating in the liquid does not interfere with the titration; *corallin* (see below, 6, *cc*) is especially recommended as the indicator. A drop of a moderately concentrated solution is sufficient to colour the liquid as well as the precipitate deep rose-red. Acid is added until the whole is milk-white. It is then boiled, and the rose tint, which again appears, is destroyed by a few drops of acid. The neutralisation is complete if after boiling for some minutes the mixture is milk-white, or at the most has a yellowish tinge. The number of c.c. of acid used is now subtracted from that of the soda originally added, and the difference represents the amount of alkali which was required by the phosphoric acid, or the phosphate, to form the basic salt $3NaO,PO_5$.

5. For all ordinary analyses by saturation, *tincture of litmus* prepared (Vol. I. p. 102, § 65, 2) from good litmus answers perfectly. For especially accurate investigation, a litmus tincture made from purified litmus or in a different manner is recommended for various reasons.

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* A. SCHEURER-KESTNER, Compt. rend. 86, 1024; Chem. Centr. 1878, p. 423.

† Würzburger medicin. Zeitschr. 1861, 93.

‡ Journ. f. prakt. Chem. N.F. 6, 16.

§ Zeitschr. f. anal. Chem. 15, 417.

BERTHELOT and A. DE FLEURIEU[*] prepare the solution by adding pure dilute sulphuric acid to concentrated aqueous solution of litmus to acid reaction, removing the carbonic acid by boiling, adding baryta water to alkaline reaction, passing a little carbonic acid through, boiling, filtering, and adding $\frac{1}{10}$th its volume of alcohol to the filtrate. WARTHA,[†] who remarks that litmus often contains indigo, recommends the following method for the preparation of the pure colouring matter of litmus. Commercial litmus is shaken up with ordinary spirit, and the cloudy, bluish-violet liquor separated, and distilled water poured on to the residue of litmus that has been treated in this way; after the mixture has been allowed to remain for twenty-four to forty-eight hours, the deeply coloured liquid is poured off and evaporated down on a water-bath; the residue is then treated repeatedly with absolute alcohol containing a little acetic acid and again evaporated. In this way the residue becomes dry and brittle; it is powdered, and the brown powder is extracted with absolute alcohol acidified with acetic acid; this removes a large quantity of a scarlet colouring matter, which is not rendered blue by alkalies, but purplish red. The brownish-red powder insoluble in absolute alcohol is dissolved in water, the solution filtered and evaporated to dryness on a water-bath; finally all the acetic acid is driven off by repeatedly moistening with absolute alcohol and drying; the residue, when dissolved in water, yields a very sensitive litmus tincture. According to F. MOHR,[‡] the litmus should be exhausted with hot distilled water, the filtered solution evaporated, supersaturated with acetic acid (whereby carbonic acid is liberated), and again evaporated to the consistence of a thick extract. The mass is then transferred to a flask, and a rather large quantity of 90 per cent. spirit poured on to it; this precipitates blue colouring matter, whilst a red coloured substance and acetate of potassa remain in solution. The colouring matter is collected on a filter, washed with spirit, dissolved in warm water, and the solution filtered.

6. Instead of tincture of litmus, various other colouring matters can be employed to indicate the first excess of alkali when neutralising an acid. On the whole, the author gives the preference to litmus over all other indicators, although occasionally other indicators have advantages over it. In the selection of these, it must be borne in mind that different individuals differ in their power of distinguishing colour, and that some eyes are better adapted to see one tint of colour and some another. Moreover, the source of illumination has an influence, and indicators which do not offer any advantages by daylight, may be preferable by gas-light or lamp-light. It should be remembered that every one who discovers a new indicator has his own special liking for it, and, further, that use has a great influence, so that it can readily be understood how the literature of indicators may gradually expand to a considerable extent. In the following only the most essential of the many other indicators proposed are noticed.

aa. Tincture of Cochineal.[§]—This has been recommended for acidimetric and alkalimetric purposes by C. LUCKOW.* It has a deep ruby-red colour; on gradually diluting it with the purest distilled water it turns orange, and afterwards orange-yellow; by gaslight this appears colourless. In the presence of the smallest amount of caustic or carbonated alkali, or of caustic alkaline earth, or of dissolved alkaline earthy carbonate, the colour changes to carmine or violet-carmine. Tincture of cochineal is used with advantage whenever, in the determination of a free acid, carbonic acid comes into play, whether the liquid itself contains it, or whether the soda solution has gradually absorbed it. For whilst the presence of carbonic acid interferes with the detection of the first trace of excess of alkali when tincture of litmus is used, and renders it necessary to drive off the carbonic acid by heating the liquid, this is not the case when tincture of cochineal is used, the colouring matter of the latter being an acid, namely, carminic acid. Carbonic acid, however, is not entirely without influence, as the first drop of normal soda solution gives a violet tinge to distilled water coloured with cochineal; but this is not the case if carbonic acid water is first added. Salts of ammonia have no prejudicial effect. If salts of acetic acid or of iron or alumina are present, tincture of cochineal cannot be used.

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[*] Zeitschr. f. anal. Chem. 5, 100.

[†] Ber. deutsch. chem. Ges. 9, 217; Zeitschr. f. anal. Chem. 15, 322.

[‡] Lehrbuch der Titrirmethode, 5th ed. p. 724.

[§] The tincture is prepared as follows:—Macerate with frequent shaking about grams of good cochineal in powder with ¼ litre of a mixture of 3 or 4 vols. disilled water and 1 vol. alcohol, and filter through Swedish paper. It keeps well in losed bottles.

In alkaline solution the carminic acid is gradually decomposed by the oxygen of the atmosphere, so that an alkaline solution coloured violet by cochineal becomes first of all discoloured, and then colourless.

bb. Extract or Tincture of Logwood.—These have been recommended by POHL † and by WILDENSTEIN.‡ The former uses commercial liquid extract of logwood of about 1·036 sp. gr. The latter employs for the preparation of the tincture a piece of logwood of the best quality, without splits or cracks, takes very fine shavings from the inner surface by means of a plane, boils them with distilled water, and mixes 1 vol. of the concentrated decoction with 1 or 2 vols. of spirit. The tincture should be kept from the light. Commercial ground *campeachy wood* is not available for the preparation of the tincture, as the desired red colour is given to it in grinding by moistening with calcareous spring water.

If neutral liquids are mixed with extract or tincture of logwood, they acquire a yellow colour, which, on the addition of acids, remains the same or becomes slightly paler. If they are neutralised by an alkaline solution, the first trace of alkali in excess is recognised by the deep-red or purplish-violet coloration of the liquid; this change is very characteristic, and sharply perceptible even by lamp-light. POHL especially recommends extract of logwood for the determination of free acids in wine (even in red wine if sufficiently diluted), and in must. If the oxides of the heavy metals (iron, copper, lead, tin, antimony, &c.) are present, even in traces, logwood tincture cannot be used.

It should be especially noted that the colouring matter is very rapidly oxidised in an alkaline solution by the action of atmospheric oxygen.

cc. Rosolic Acid (Corallin).—This is prepared by heating for 5 or 6 hours, at 140°—150°, 1 part by weight of crystallised oxalic acid, 1½ part by weight of crystallised colourless phenol, and 2 parts by weight of sulphuric acid; the materials are heated in an oil-bath in a flask provided with a reflux condenser, and the dark semi-fluid product is poured into a large quantity of water. The rosolic acid is thus obtained as a resinous mass which is boiled with water until the odour of phenol disappears, and is then thoroughly washed with cold water. The product thus obtained—although not pure rosolic acid—is well adapted for the preparation of the indicator; for this purpose it is dissolved in spirit, and the solution filtered. The deep red-violet liquid colours water reddish-yellow. On adding a drop of normal acid, the liquid becomes colourless or very pale yellow, and of a beautiful reddish-violet colour with the slightest excess of alkali. A liquid thus coloured also becomes pale yellow on the addition of water containing carbonic acid. Corallin is a very good indicator if free acids are to be neutralised by caustic alkalies; the presence of carbonic acid, however, acts prejudicially. The presence of neutral ammonia salts does not interfere with the reaction.

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* Journ. f. prakt. Chem. 84, 424; Zeitschr. f. anal. Chem. 1, 386.

† Journ. f. prakt. Chem. 81, 59.

‡ Zeitschr. f. anal. Chem. 2, 9.

dd. Phenolphthaleïn.—This colouring matter, discovered by BAEYER,* has been recommended by E. LUCK† as an indicator in acidimetry. It is prepared by heating 10 parts of phenol with 5 parts of phthalic anhydride and 4 parts of concentrated sulphuric acid at 120°—130° for several hours; the red mass thus obtained is first boiled with water, and the resinous product left is then boiled with benzene, whereby it becomes changed to a yellowish-white powder. The indicator is prepared by dissolving 1 part of the phenolphthaleïn in 30 parts of 90 per cent. alcohol. 1 or at the most 2 drops of the solution are added to 80—100 c.c. of the solution to be titrated. If the solution is acid, it is opalescent at first, but becomes perfectly clear on stirring. Water or dilute acid is not coloured by the indicator; but if an alkali is added, the solution acquires an intense purplish-red colour as soon as there is the slightest excess of alkali. On adding a drop of acid, the liquid again becomes colourless. The solution reddened by alkali is also deprived of colour by carbonic acid; so that the presence of carbonic acid interferes with the reaction. The indicator cannot be used if ammonia salts are present.

ee. Tropaeolin.—Under this name various colours, discovered by O. N. WITT, have come into the market. Two of these, numbers 00 and 000, have been recommended by W. v. MILLER‡ as indicators. The solution of tropaeolin 00 is either a 0·05 per cent. aqueous solution, or a cold saturated alcoholic solution, and if either 2 c.c. of the aqueous, or a few drops of the alcoholic, solution of tropaeolin are added to 50 c.c. of water, a bright yellow solution is obtained, which is not changed either by acid carbonates or by free carbonic acid; but on the addition of a dilute mineral acid (or of certain organic acids, especially oxalic acid) it becomes yellowish-red, and, with a larger excess of acid, red. On adding an alkali, the red colour is again changed to yellow. MILLER recommends this indicator especially because carbonic acid has no influence on the change of colour, and because with tropaeolin solution (preferably the alcoholic) free acids can be recognised and estimated in the presence of metallic salts. Ammonia salts do not act prejudicially in the application of tropaeolin 00.

Tropaeolin 000 serves for the detection of free alkalies in the same way that tropaeolin 00 does for free acids. A drop of a cold saturated aqueous solution of tropaeolin 000 is added to the acid solution that is to be titrated. This causes a scarcely perceptible yellow coloration, which, on the addition of an alkali, becomes red directly there is an excess of the latter. The transition is distinct and sharp. Ammonia salts have no prejudicial effect. In the presence of carbonic acid, tropaeolin 000 cannot be used.

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* Ber. deutsch. chem. Ges. 4, 658 (1871).

† Zeitschr. f. anal. Chem. 16, 332.

‡ Ber. deutsch. chem. Ges. 11, 460; Zeitschr. f. anal. Chem. 17, 474.

IV. APPLICATION OF THE ACIDIMETRIC PRINCIPLE TO THE DETERMINATION OF COMBINED ACIDS.

a. The acidimetric principle may often be employed also for the determination of acids in combination with bases, if solution of soda (or of carbonate of soda) precipitates the latter completely, and in a state of purity. For instance, acetic acid in iron mordant, or in verdigris, may be estimated in this way:—The solution is precipitated with a measured quantity of normal solution of soda in excess (or a solution of carbonate of soda of known strength), boiled, filtered, washed, the filtrate concentrated, and normal acid added to acid reaction. The mixture is then boiled to expel the carbonic acid which the soda solution may have absorbed in the process of evaporation, coloured with litmus, and titrated with solution of soda until a blue tint is imparted to the liquid. The amount of standard acid used is subtracted from the total quantity of soda solution consumed in the experiment, and the difference gives the quantity of soda solution neutralised by the acid contained in the substance, in combination as well as in the free state. Of course, trustworthy results can be expected only where no basic salt is thrown down by the soda solution.

b. If a salt contains a base which is precipitable by sulphuretted hydrogen from an acid solution, and an acid which is not volatile, and does not act on sulphuretted hydrogen, this gas is passed (WALCOTT GIBBS*) into the boiling solution to complete saturation. After the precipitate has been filtered off and washed with hot water, the filtrate is allowed to cool, diluted to a litre or a half litre, and the free acid determined in an aliquot portion of it. If the acid is nitric or hydrochloric, Rochelle salt (tartrate of potassa and soda) is added. This prevents the decomposing action of the nitric acid on the sulphuretted hydrogen, and the volatilisation of the acid. The presence of the salts of the alkalies and alkaline earths is without influence; but salts of iron or alumina must be absent. The method can, of course, only give accurate results if the precipitated sulphides of the metals are pure, that is, free from any of the acids present.

c. If the sulphuric acid in alum is to be determined by acidimetry, it cannot be done by the direct addition of normal soda solution to saturation, as in this way basic sulphate of alumina would be precipitated, and, therefore, the quantity of soda solution employed would not correspond with the sulphuric acid present. This difficulty may be avoided by employing the method proposed by E. ERLENMEYER and LEWINSTEIN. Chloride of barium in excess is added, and then the soda solution, which precipitates pure hydrate of alumina from the solution of chloride of aluminium thus produced.

If the alumina salt—as is the case with pure alum—is a neutral salt, and no free acid is present, the amount of acid found gives the amount of alumina by calculating 1 eq. of alumina for 3 eq. of acid. According to W. Stein,[*] the easiest method of ascertaining whether an alumina salt contains free acid is by means of ultramarine paper; this is rendered colourless by free acid.[†]

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* Sill. Amer. Journ. [ii.] 44, 207; Zeitschr. f. anal. Chem. 7, 94.

Satisfactory results are also obtained by (as proposed for the same purpose by Erlenmeyer and Lewinstein) the use of freshly precipitated, carefully washed ammonio-phosphate of magnesia, which—added in excess—is decomposed by neutral alumina salts in such a way that a solution with a neutral reaction is produced. The most convenient solution for testing is, however, the alcoholic solution of tropaeolin 00 (p. 200).

d. The method in which in many cases a slight excess of some particular acid can be estimated by means of acidimetry used along with the gravimetric determination will be described farther on, with the analysis of the acetates of lime and lead.

C. Estimation by Saturating the Free Acid with an Alkaline Liquid without using a Colouring Matter as Indicator.

§ 216.

Instead of estimating free acid by a solution of soda of known strength, and determining the point of neutralisation by means of tincture of litmus, an ammoniacal solution of oxide of copper may be used for the purpose, as recommended by Kiefer;[‡] in this case, the point of neutralisation is known by the turbidity observed as soon as the free acid present is completely neutralised. The copper solution is prepared by adding solution of ammonia to an aqueous solution of sulphate of copper, until the precipitate of basic salt which forms at first is *just* redissolved. After determining the strength of the solution by normal sulphuric or hydrochloric acid (not oxalic), it may be employed for the estimation of all the stronger acids (with the exception of oxalic acid), provided the solutions are clear. As the basic salt of copper, in the precipitation of which the final reaction consists, is not insoluble in the ammonia salt produced, it cannot be found until the solution is saturated with it, its solubility, moreover, depending on the degree of concentration, and on the presence of other salts, especially of ammonia salts (Carey Lea[§]). On this account, the method cannot boast of scientific accuracy, but as the variations occasioned by the causes mentioned are inconsiderable,[||] the process retains its applicability to technical purposes, for which, indeed, it was originally proposed. Kiefer's method is especially useful in cases in which free acid is to be determined in presence of a neutral metallic salt with acid reaction—for example, free sulphuric acid in mother liquors of sulphate of copper or sulphate of zinc, &c. It is advisable to redetermine the strength of the ammoniacal copper solution before every fresh series of experiments.

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[*] Zeitschr. f. anal. Chem. 5, 289.

[†] Stein (Zeitschr. f. anal. Chem. 8, 450) prepares this paper by stirring ultramarine of special quality with carragheen (Iceland moss) jelly (1 part of Iceland moss boiled with 30—40 parts of water), and spreading it evenly with a broad brush on unsized paper. It is advisable to prepare both a paler and a darker paper. The ultramarine is suitable if the paper prepared with it is easily rendered colourless by dilute sulphuric acid, but is not altered by a neutral solution of alum which has been purified by repeated precipitation by alcohol.

[‡] Annal. d. Chem. u. Pharm. 93, 386.

[§] Chem. News, 1861, 4, 195.

[||] Compare the author's experiments on the subject in the Zeitschr. f. anal. Chem. 1, 108.

D. Estimation by Weighing the Carbonic Acid Expelled by the Free Acid from Bicarbonate of Soda.

§ 217.

A portion of the acid under examination is weighed in the flask *A* (fig. 94), and if the acid is concentrated, water is added; the liquid should occupy about ⅓ of the flask. A small glass tube is filled compactly with bicarbonate of soda or potassa,* and is suspended by a thread in the flask *A*, by pressing the thread between the cork and the neck of the flask, the apparatus being arranged exactly in the manner described in § 139, *d*, Vol. I. p. 337. After it has been tared on the balance, the cork is raised so as to allow the thread and the small tube to which it is attached to drop into the flask *A*, the cork being inserted again air-tight the instant the thread is released. A rapid evolution of carbonic acid at once takes place, and continues for some time at a uniform rate, then diminishes, and ultimately ceases altogether. When this point is reached, the flask *A* is put into water which is so hot that you can only just bear your finger in it for a short time (temp. 50° to 55°). When the renewed evolution of carbonic acid to which this gives rise has again ceased, the wax stopper, *b*, on the tube, *a*, is opened a little, the flask removed from the water-bath, and suction applied to *d*, by means of an india-rubber tube, until all the carbonic acid still remaining in the apparatus is displaced by atmospheric air. For the best method of applying suction see Vol. I. p. 337. When cold, the apparatus is replaced on the balance, and weights added until the equilibrium is restored. The sum of these gives the quantity of carbonic acid expelled. For each eq. acid used, 2 eq. carbonic acid are obtained; thus, $NaO,HO,2CO_2 + HO,NO_5 = NaO,NO_5 + 2CO_2 + 2HO$. The results are satisfactory.† The quantity of the acid should, when practicable, be so adjusted as to yield 1 to 2 grams of carbonic acid. This method is preferable to that described in B, only in the case of

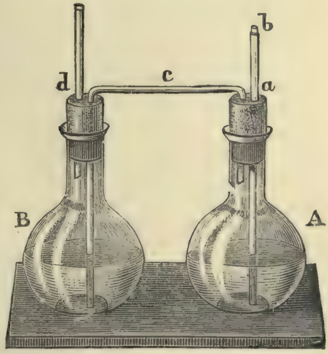

Fig. 94.

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* The bicarbonate used may contain chloride of sodium, sulphate, &c.; but it must be quite free from neutral carbonate, and the quantity must be more than sufficient to saturate the acid in the flask.

† Comp. New Methods for Testing Potash and Soda, and of Determining the Commercial Value of Acids and Manganese, by Drs. R. Fresenius and H. Will. Edited by J. L. Bullock. Taylor and Walton, 1843.

coloured liquids, in which the litmus reaction cannot be distinctly observed. Instead of determining the carbonic acid by the loss of weight of the apparatus here mentioned, the method described Vol. I. p. 340, can be adopted.

E. Methods relating to Particular Acids.

Determination of the Composition of Glacial Acetic Acid from its Solidifying Point.

Fr. Rüdorff* recommends the valuation of the most concentrated acetic acid by means of its solidifying point. The annexed table, based on his results, shows the relation of the temperature of solidification to the amount of hydrated acetic acid :—

100 parts of hydrated acetic acid are mixed with—	100 parts of the mixture contain—	Solidifying temperature.
0·0 water	0·0 water	+ 16·70° C.
0·5 "	0·497 "	15·65 "
1·0 "	0·990 "	14·80 "
1·5 "	1·477 "	14·00 "
2·0 "	1·961 "	13·25 "
3·0 "	2·912 "	11·95 "
4·0 "	3·846 "	10·50 "
5·0 "	4·761 "	9·40 "
6·0 "	5·660 "	8·20 "
7·0 "	6·542 "	7·10 "
8·0 "	7·407 "	6·25 "
9·0 "	8·257 "	5·30 "
10·0 "	9·090 "	4·30 "
11·0 "	9·910 "	3·60 "
12·0 "	10·774 "	2·70 "
15·0 "	13·043 "	0·20 "
18·0 "	15·324 "	− 2·60 "
21·0 "	17·355 "	5·10 "
24·0 "	19·354 "	7·40 "

In determining the solidifying point, it is necessary to take care that only a little of the acetic acid crystallises. This is done with the greatest certainty by cooling the fluid about 1° below the approximately determined solidifying point, and causing the separation of the hydrated acetic acid by throwing in a small piece of solid hydrated acetic acid, and stirring with a sensitive thermometer. The temperature then rises to the solidifying point of the mixture. Small quantities of solid hydrated acetic acid are easily procured by putting a little acetic acid into a test-tube, and stirring a mixture of cold water with sal-ammoniac, nitrate of ammonia, or sulphocyanate of potassium with the tube.

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* Ber. deutsch. chem. Ges. 3, 390 ; Zeitschr. f. anal. Chem. 10, 106.

2. ESTIMATION OF FREE ALKALI AND ALKALINE CARBONATE (ALKALIMETRY).

A. Estimation of Potassa, Soda, or Ammonia, Carbonate of Potassa, Carbonate of Soda, from the Specific Gravity of their Solutions.

§ 218.

In pure or nearly pure solutions of the hydrates or carbonates of potassa or soda, or of ammonia in water, the percentage of alkali may be estimated from the specific gravity of the solution.

Table I.

Of the amounts of Potash and Hydrate of Potash in Potash Solution at various specific gravities, by SCHIFF and TÜNNERMANN, calculated by GERLACH.*

Amount in 100 parts by weight of the solution.	Potash, specific gravity at 15° C.	Potash hydrate, KO,HO, specific gravity at 15° C.	Amount in 100 parts by weight of the solution.	Potash, specific gravity at 15° C.	Potash hydrate, KO,HO, specific gravity at 15° C.
1	1·010	1·009	36	1·455	1·361
2	1·020	1·017	37	1·460	1·374
3	1·030	1·025	38	1·475	1·387
4	1·039	1·033	39	1·490	1·400
5	1·048	1·041	40	1·504	1·411
6	1·058	1·049	41	1·522	1·425
7	1·068	1·053	42	1·539	1·438
8	1·078	1·065	43	1·564	1·450
9	1·089	1·074	44	1·570	1·462
10	1·099	1·083	45	1·584	1·475
11	1·110	1·092	46	1·600	1·488
12	1·121	1·110	47	1·615	1·499
13	1·132	1·111	48	1·630	1·511
14	1·143	1·119	49	1·645	1·527
15	1·154	1·128	50	1·660	1·539
16	1·166	1·137	51	1·676	1·552
17	1·178	1·146	52	1·690	1·565
18	1·190	1·155	53	1·705	1·578
19	1·202	1·166	54	1·720	1·590
20	1·215	1·177	55	1·733	1·604
21	1·230	1·188	56	1·746	1·618
22	1·242	1·198	57	1·762	1·630
23	1·256	1·209	58	1·780	1·641
24	1·270	1·220	59	1·795	1·655
25	1·285	1·230	60	1·810	1·667
26	1·300	1·241	61	...	1·682
27	1·312	1·252	62	...	1·695
28	1·326	1·264	63	...	1·705
29	1·340	1·278	64	...	1·718
30	1·355	1·288	65	...	1·729
31	1·370	1·300	66	...	1·740
32	1·385	1·311	67	...	1·751
33	1·403	1·324	68	...	1·768
34	1·418	1·336	69	...	1·780
35	1·431	1·349	70	...	1·790

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* Zeitschr. f. anal. Chem. 8, 279.

Table II.

Of the amounts of Soda and Hydrate of Soda in Soda Solution at various specific gravities, by SCHIFF, calculated by GERLACH.*

Amount in 100 parts by weight of the solution.	Soda, specific gravity at 15° C.	Soda hydrate, NaO,HO, specific gravity at 15° C.	Amount in 100 parts by weight of the solution.	Soda, specific gravity at 15° C.	Soda hydrate, NaO,HO, specific gravity at 15° C.
1	1·015	1·012	36	1·500	1·395
2	1·020	1·023	37	1·515	1·405
3	1·043	1·035	38	1·530	1·415
4	1·058	1·046	39	1·543	1·426
5	1·074	1·059	40	1·558	1·437
6	1·089	1·070	41	1·570	1·447
7	1·104	1·081	42	1·583	1·456
8	1·119	1·092	43	1·597	1·468
9	1·132	1·103	44	1·610	1·478
10	1·145	1·115	45	1·623	1·488
11	1·160	1·126	46	1·637	1·499
12	1·175	1·137	47	1·650	1·508
13	1·190	1·148	48	1·663	1·519
14	1·203	1·159	49	1·678	1·529
15	1·219	1·170	50	1·690	1·540
16	1·233	1·181	51	1·705	1·550
17	1·245	1·192	52	1·719	1·560
18	1·258	1·202	53	1·731	1·570
19	1·270	1·213	54	1·745	1·580
20	1·285	1·225	55	1·760	1·591
21	1·300	1·236	56	1·770	1 601
22	1·315	1·247	57	1·785	1·611
23	1·329	1·258	58	1·800	1·622
24	1·341	1·269	59	1·815	1·633
25	1·355	1·279	60	1·830	1·643
26	1·369	1·290	61	...	1·654
27	1·381	1·300	62	...	1·664
28	1·395	1·310	63	...	1·674
29	1·410	1·321	64	...	1·684
30	1·422	1·332	65	...	1·695
31	1·438	1·343	66	...	1·705
32	1·450	1·351	67	...	1·715
33	1·462	1·363	68	...	1·726
34	1·475	1·374	69	...	1·737
35	1·488	1·384	70	...	1·748

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* Zeitschr. f. anal. Chem. 8, 279.

Table III.

Of the amounts of Anhydrous Carbonates of Potassa and Soda in Aqueous Solutions at various specific gravities, by Gerlach.*

Amount in 100 parts by weight of the solution.	Carbonate of potassa, specific gravity at 15° C.	Carbonate of soda, specific gravity at 15° C.	Amount in 100 parts by weight of the solution.	Carbonate of potassa, specific gravity at 15° C.	Carbonate of soda, specific gravity at 15° C.
1	1·00914	1·01050	27	1·26787	
2	1·01829	1·02101	28	1·27893	
3	1·02743	1·03151	29	1·28999	
4	1·03658	1·04201	30	1·30105	
5	1·04572	1·05255	31	1·31261	
6	1·05513	1·06309	32	1·32417	
7	1·06454	1·07369	33	1·33573	
8	1·07396	1·08430	34	1·34729	
9	1·08337	1·09500	35	1·35885	
10	1·09278	1·10571	36	1·37082	
11	1·10258	1·11655	37	1·38279	
12	1·11238	1·12740	38	1·39476	
13	1·12219	1·13845	39	1·40673	
14	1·13199	1·14950	40	1·41870	
15	1·14179		41	1·43104	
16	1·15200		42	1·44338	
17	1·16222		43	1·44573	
18	1·17243		44	1·46807	
19	1·18265		45	1·48041	
20	1·19286		46	1·49314	
21	1·20344		47	1·50588	
22	1·21402		48	1·51861	
23	1·22459		49	1·53135	
24	1·23517		50	1·54408	
25	1·24575		51	1·55728	
26	1·25681		52	1·57048	

Table IVa.

Of the amount of Ammonia (NH_3) in Solutions of Ammonia of various specific gravities, by Carius, calculated by Gerlach.*

Amount in 100 parts by weight of the solution.	Ammonia, specific gravity at 16° C.	Amount in 100 parts by weight of the solution.	Ammonia, specific gravity at 16° C.	Amount in 100 parts by weight of the solution.	Ammonia, specific gravity at 16° C.	Amount in 100 parts by weight of the solution.	Ammonia, specific gravity at 16° C.
1	0·9959	10	0·9593	19	0·9283	28	0·9026
2	0·9915	11	0·9556	20	0·9251	29	0·9001
3	0·9873	12	0·9520	21	0·9221	30	0·8976
4	0·9831	13	0·9484	22	0·9191	31	0·8953
5	0·9790	14	0·9449	23	0·9162	32	0·8929
6	0·9749	15	0·9414	24	0·9133	33	0·8907
7	0·9709	16	0·9380	25	0·9106	34	0·8885
8	0·9670	17	0·9347	26	0·9078	35	0·8864
9	0·9631	18	0·9314	27	0·9052	36	0·8844

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* Zeitschr. f. anal. Chem. 8, 279.

Table IVb.

Percentages of Ammonia (NH_3) corresponding to different specific gravities of Solution of Ammonia at 16° C. (J. OTTO) for weaker Solutions.

Specific gravity.	Percentage of ammonia.	Specific gravity.	Percentage of ammonia.	Specific gravity.	Percentage of ammonia.
0·9517	12·000	0·9607	9·625	0·9697	7·250
0·9521	11·875	0·9612	9·500	0·9702	7·125
0·9526	11·750	0·9616	9·375	0·9707	7·000
0·9531	11·625	0·9621	9·250	0·9711	6·875
0·9536	11·500	0·9626	9·125	0·9716	6·750
0·9540	11·375	0·9631	9·000	0·9721	6·625
0·9545	11·250	0·9636	8·875	0·9726	6·500
0·9550	11·125	0·9641	8·750	0·9730	6·375
0·9555	11·000	0·9645	8·625	0·9735	6·250
0·9556	10·950	0·9650	8·500	0·9740	6·125
0·9559	10·875	0·9654	8·375	0·9745	6·000
0·9564	10·750	0·9659	8·250	0·9749	5·875
0·9569	10·625	0·9664	8·125	0·9754	5·750
0·9574	10·500	0·9669	8·000	0·9759	5·625
0·9578	10·375	0·9673	7·875	0·9764	5·500
0·9583	10·250	0·9678	7·750	0·9768	5·375
0·9588	10·125	0·9683	7·625	0·9773	5·250
0·9593	10·000	0·9688	7·500	0·9778	5·125
0·9597	9·875	0·9692	7·375	0·9783	5·000
0·9602	9·750				

B. Estimation of the total Amount of Carbonated and Caustic Alkali present in a Substance.

I. Volumetric Methods.

a. Method of DESCROIZILLES *and* GAY-LUSSAC, *slightly modified.*

§ 219.

The principle of this method is the converse of that on which the acidimetric method, described § 215, is based; that is, if we know the quantity of an acid of known strength required to saturate an unknown quantity of caustic potassa or soda, or of carbonate of potassa or soda, we may readily calculate from this the amount of alkali present.

The process requires only *one* solution of known strength, namely, a standard sulphuric acid.

This is now almost universally made of such a strength that 50 c.c. will saturate 5 grams of pure anhydrous carbonate of soda.

The following is the most simple way of preparing it:—

a. About 60 grams of concentrated sulphuric acid is mixed with 500 c.c., or 120 grams with 1000 c.c. of water, and the mixture allowed to cool.

b. 5 grams of pure anhydrous carbonate of soda is accurately weighed, transferred to a flask, dissolved in about 200 c.c. water, and the solution coloured distinctly blue with a measured quantity (about 1 c.c.) of violet tincture of litmus (see Mohr, this vol. p. 198).

> N.B. This is addressed to those only who are not accustomed to weigh on delicate balances. Where chemical balances are used, as is usually the case in chemical laboratories, it is far better to ignite gently in a platinum crucible from 4·5 to 5 grams of carbonate of soda, allow it to cool under the desiccator, and weigh accurately. The carbonate is then transferred to the flask, and the crucible weighed; in this way the exact quantity of carbonate of soda in the flask is known with the greatest accuracy. An experienced chemist, accustomed to the use of a delicate balance, can perform this process more easily and quickly than the other; and the results, also, are far more trustworthy, as the substance is weighed in a covered crucible. If several portions are to be weighed one after another, the ignited salt is transferred while still hot to a test-tube provided with stopper, weighed, a suitable quantity shaken out, and the tube weighed again, &c. The alkali to be examined is afterwards weighed in the same manner as the pure carbonate of soda.

c. A burette (preferably one holding 50 c.c.) is filled up to the zero mark with the cold dilute acid, which is then allowed to flow into the solution of soda, until saturation is complete (see below). It is better to make this experiment twice. If the carbonate of soda taken was not exactly 5 grams, it is necessary to calculate from the results obtained how much acid 5 grams would have required.

d. The remainder of the acid is diluted with water so that exactly 50 c.c. are required to saturate 5 grams of carbonate of soda. Suppose in the experiments it took 45 c.c. of the acid to saturate 5 grams of carbonate of soda, 5 volumes of water must be added to each 45 volumes of the acid. The dilution is most conveniently effected in the manner described this vol. p. 190. It is of the greatest importance to test the dilute acid once more in the way described above.

e. The standard acid thus prepared must be kept in well-stoppered bottles, and shaken before every fresh series of experiments (p. 191). This standard acid serves for the examination of common soda, pearlash, and caustic alkalies; the number of half c.c. used giving directly the percentage of alkaline carbonate or caustic alkali present, provided the experiment is made with a weighed quantity of the substance equivalent to 5 grams of carbonate of soda.

The following table shows the equivalent quantities:—

50 c.c. of the standard	acid	saturates	5·000	grams	of carbonate of soda.
,,	,,	,,	2·926	,,	soda.
,,	,,	,,	6·517	,,	carbonate of potassa.
,,	,,	,,	4·443	,,	potassa.

Accordingly, if 6·517 grams of a sample of pearlash are taken, the number of half c.c. of the standard acid used gives directly the percentage of alkali, expressed as carbonate of potassa; if 4·443 grams are taken, the number of half c.c. of the standard acid used gives the percentage of alkali, expressed as anhydrous caustic potassa, &c.

In the examination of substances poor in carbonated or caustic alkalies, a multiple of (twice, three times, ten times, &c.) the quantities given above should be used, the number of half c.c. of the standard acid required for neutralisation being afterwards divided by the corresponding number.

f. With respect to the determination of the point of saturation, this is easy with caustic alkalies; but in the case of alkaline carbonates, the liberated carbonic acid, which imparts a wine-red colour to the liquid, causes some difficulty. This may be overcome in two ways.

a. When sufficient of the standard acid has been added to impart a wine-red colour to the cold, or, it may be, already heated, solution of soda or pearlash contained in a flask, the liquid is heated to ebullition, with frequent shaking, when its colour will change from red to blue as the carbonic acid escapes. If some more standard acid is now added to the nearly boiling liquid, the vessel being occasionally heated by the lamp, it is very easy to hit the exact point of saturation, or, more correctly speaking, the commencement of supersaturation, which is indicated by the colour of the liquid becoming red, slightly inclining to yellow.

β. The point of saturation may be ascertained, also, without heating, although not with the same degree of accuracy; the flask, however, in this case must not be too small. After every fresh addition of standard acid, the liquid must be carefully and vigorously shaken, the addition of acid being continued as long as the red colour of the liquid continues to show a tint of violet. When the point of saturation is nigh, the acid must be added more cautiously, two drops at a time, and, after every fresh addition, a glass rod should be dipped into the liquid, and one or, better, two spots made with it on a slip of fine blue litmus-paper, the volume being read off each time, and the number marked between the spots. This is continued until the spots on the litmus-paper appear decidedly red. The paper is then allowed to dry, the lowest number being taken as correct where the spots between which it is marked just remain red.

It should be borne in mind, as a rule, that the standard acid must be tested by the same method which is subsequently used in the actual analysis. For this reason, a standard sulphuric, hydrochloric, or oxalic acid, as prepared according to the directions of § 215, cannot be employed for the direct and immediate estimation of the alkalies.

b. F. MOHR'S *Method.*

§ 220.

Instead of titrating the alkalies directly by means of an acid of known strength, we may estimate them also, as proposed first by F. MOHR,[*] by supersaturating with standard acid, expelling the carbonic acid by boiling, and finally titrating with soda solution the excess of standard acid added.

This process gives very good results, and is therefore particularly well suited for scientific investigations. It requires the standard solutions mentioned in § 215, namely, a normal acid and normal soda solution. Each of these liquids is contained in its own burette.

The alkali or hydrate of the alkali is dissolved in water, and the solution coloured pale blue with a measured quantity of tincture of litmus.[†] As much of the normal acid is now run in as will suffice to impart a violet tint to the liquid, which is then boiled and more acid added, until the colour is distinctly yellowish red, then a further quantity, to the next c.c. line. The alkali is now decidedly supersaturated; and the last traces of carbonic acid are removed by boiling, shaking, blowing into the flask, and finally sucking out the air.

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[*] Annal. d. Chem. u. Pharm. 86, 129.

[†] For other indicators see p. 198.

Standard solution of soda is now added, drop by drop, until the colour just appears light blue. If the liquid is free from carbonic acid, and only slightly coloured with litmus, there is no difficulty in determining the exact point at which the reaction is completed; if, however, the reverse is the case, it cannot be determined with accuracy, as the blue tint just imparted to the fluid by the solution of soda continues to change again to violet for some time.

If the standard soda solution and the normal acid are of corresponding strength, the number of c.c. of the soda solution used is simply deducted from the number of c.c. of the acid; the difference gives the quantity of acid neutralised by the alkali present in the sample. If the two standard solutions are not of corresponding strength, the excess of acid added, and subsequently neutralised by the soda solution, is calculated from the known ratio the one bears to the other.

If $\frac{1}{10}$ eq. number $(H=1)$ of grams of the alkali to be valued has been weighed out, that is, of soda 5·304 grams, of pearlash 6·913 grams, the number of c.c. of the normal acid used expresses directly the percentage of carbonate of soda or carbonate of potassa contained in the sample examined; since 100 c.c. of the normal acid, containing $\frac{1}{10}$ gram eq. of acid will just suffice to neutralise $\frac{1}{10}$ gram eq. of pure carbonate of soda or carbonate of potassa. If any other quantity of the alkali has been weighed out, a simple calculation will give the result in the desired form.

To make this simple calculation quite clear for all possible cases, one of the most complicated kind has been selected, proceeding on the supposition that the soda solution does not correspond in strength with the normal acid, but that 1·1 c.c. of the soda solution neutralises 1 c.c. of the normal acid; and that instead of $\frac{1}{10}$ gram eq., 2·12 grams of impure carbonate of potash has been weighed out.

The quantity of acid added was 26 c.c.; the excess required 2·1 c.c. of soda solution for neutralisation. The proportion

$$1{\cdot}1 : 1 :: 2{\cdot}1 : x \qquad x = 1{\cdot}91$$

shows that the excess of acid was 1·91 c.c.; $26 - 1{\cdot}91 = 24{\cdot}09$ c.c. of the acid have accordingly been consumed by the carbonate of potash. The proportion

$$2{\cdot}12 : 24{\cdot}09 :: 6{\cdot}913\ (\tfrac{1}{10}\text{ eq. } KO,CO_2) : x \qquad x = 78{\cdot}55$$

shows that the impure carbonate of potash contains 78·55 per cent. of the pure carbonate.

II. Gravimetric Method of FRESENIUS and WILL.*

§ 221.

In this method the quantity of alkaline carbonate contained in a sample of commercial alkali is calculated from the amount of carbonic acid disengaged from it. It is necessary, therefore, not only that all the available alkali should be present in the form of the neutral carbonate, but also that the substance should contain no other carbonate. If the sample under examination does not fulfil these conditions, it must be treated in such a manner as to bring them about.

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* Comp. the pamphlet mentioned in the foot-note, p. 203, where the method will be found described in detail.

If the substance to be examined contains alkaline bicarbonate (which gives off carbonic acid on ignition), it must be ignited before the amount of carbonic acid in it is determined. If, on the other hand, it contains caustic alkali (which yields a filtrate with an alkaline reaction after the addition of an excess of chloride of barium), the quantity that has been weighed out is heated with about its own weight of quartz sand, about $\frac{1}{3}$ of its weight of powdered carbonate of ammonia and as much water as the mass will absorb, until all the water is driven off; the carbonic acid is then determined in the residue thus obtained.

The determination of the carbonic acid is effected in the way described Vol. I. p. 337, *aa* (other methods may of course be adopted; for instance, that given in Vol. I. p. 340, *e*). The first is more suitable for technical purposes; the latter for scientific investigations.

If 6·285 grams of a substance containing carbonate of potassa, or 4·822 grams of one containing carbonate of soda are weighed out, it is only necessary to divide the number of centigrams of carbonic acid found by 2, in order to find, without further calculation, the percentage of carbonate of potassa or carbonate of soda in the substance that has been examined.

It is of course evident that neither this method nor the alkalimetric method can be used for determining carbonate of potassa if it is mixed with carbonate of soda; the results are accurate only when carbonate of potassa alone or carbonate of soda alone (besides other neutral salts) is present.

The special points to be noted in the analysis of pearlash or soda-ash by this method will be noticed later on (§ 224 and § 229).

C. Determination of the Caustic Alkali which is present along with Carbonate.

§ 222.

a. When we have to estimate both the caustic and carbonated alkali in mixtures of carbonate and hydrate of potash, or of carbonate and hydrate of soda, the method described in § 219 or in § 220 may be combined with the one given in § 221; that is, determining by one of the former the total amount of caustic and carbonated alkali expressed in per-cents of carbonate of soda or carbonate of potassa, and estimating by § 221—of course without previous treatment with carbonate of ammonia—the quantity of carbonic acid, and therefore also of alkaline carbonate. The difference between the results of the two determinations indicates the quantity of alkaline carbonate corresponding with the caustic alkali present. To calculate the carbonate of soda into anhydrous caustic soda, it is multiplied by 0·5852; to calculate it into hydrate of soda, it is multiplied by 0·7549; to calculate the carbonate of potassa into anhydrous caustic potassa, it is multiplied by 0·6818; to calculate it into hydrate of potassa, it is multiplied by 0·8119.

b. It will be readily seen that this object may also be attained solely by the method given in § 221, by directly determining the carbonic acid in *one* weighed sample, and in *another* after treatment with carbonate of ammonia.

c. The same object may also be attained in a purely volumetric way, by the aid of the principle which has already been made use of for testing commercial carbonate of soda for the caustic alkali.

Weigh out $\frac{3}{10}$ gram eq. of the substance, that is, of potashes 20·74 grams, of soda 15·912 grams; this is dissolved in water, in a flask holding 300 c.c., filled up to the mark, shaken, and the liquid allowed to settle out of contact with the air; two portions of 100 c.c. each are then taken out. In the one portion the total quantity of the carbonated and caustic alkali is determined, as directed in § 220; the number of c.c. of normal acid used expressing the amount of caustic alkali + alkaline carbonate, in per-cents of the latter. The other portion is transferred to a measuring flask holding 500 c.c.; 200 c.c. of water is added, and then solution of chloride of barium as long as a precipitate is formed; water is added up to the mark, the whole shaken, allowed to deposit out of contact of air,* 250 c.c. of the supernatant clear liquid—which now contains caustic baryta in quantity corresponding with the caustic alkali present in the sample—is measured off, some tincture of litmus added, and then normal hydrochloric acid to acid reaction. The excess of acid is now titrated by normal solution of soda, and in this way the number of c.c. of normal acid corresponding with the caustic baryta is found. This must be multiplied by 2 (as only one-half of the second portion has been employed in the experiment); the result gives the percentage of caustic alkali, expressed as carbonate of soda or potassa. This number is deducted from the percentage obtained in the first experiment; the difference gives the quantity of carbonate of potassa or soda present as such. To calculate the caustic alkali into the anhydrous or hydrated state, it is only necessary to multiply by the numbers given in *a*.

3. Estimation of Alkaline Earths by the Alkalimetric Method.

§ 223.

Alkaline earths, whether in the caustic state or in the form of carbonates, may also be estimated by means of a standard acid. Standard sulphuric acid may be used for the estimation of magnesia; standard hydrochloric or nitric acid for that of baryta, strontia, and lime. Normal nitric acid can be easily prepared by the use of normal soda solution, and has the advantage over normal hydrochloric acid that a solution containing free nitric acid is less likely to lose acid on boiling than a liquid containing free hydrochloric acid. However, if the operation be conducted as it should be, that is if the excess of acid is only very small when the liquid is heated to boiling, there is no fear of loss even if hydrochloric acid is employed.

If the alkaline earth to be estimated is in the caustic state, a definite quantity is weighed out, water added, and then, from a burette, normal hydrochloric or nitric acid, until dissolution takes place, and the liquid, coloured with litmus, appears red; soda solution is now added until the colour just changes to blue; the soda solution added is deducted from the acid, and the result calculated by the proportion—

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* Filtering through a dry filter causes the caustic alkali to come out rather too low, as the paper retains caustic baryta (A. Müller, Journ. f. prakt. Chem. 83, 384; Zeitschr. f. anal. Chem. 1, 84).

1000 c.c. : the number of c.c. of acid used : :
76·5 (eq. baryta), 51·75 (eq. strontia), 28 (eq. lime) or 20 (eq. magnesia)
: x (grams of baryta, strontia, lime, or magnesia).

Should there be a failure the first time in determining the exact point at which the solution turns blue, another c.c. of the acid is added, and then solution of soda again until blue.

In the case of carbonates of the alkaline earths, a weighed quantity of the sample is heated with water in a flask, and normal hydrochloric or nitric acid added from the burette in small portions at a time. When the substance is dissolved, and the acid is consequently in excess, tincture of litmus is added, and then normal soda solution, until only a small excess of free acid remains, say 0·5 or 1 c.c. The liquid is now heated to boiling, shaken, and the boiling continued for some minutes so as to expel the carbonic acid completely from the liquid and flask; finally, soda is added until just blue. 1000 c.c. of the normal acid correspond with 98·5 grams of carbonate of baryta, 73·75 grams of carbonate of strontia, 50 grams of carbonate of lime, or 42 grams of carbonate of magnesia.

By weighing off the $\frac{1}{10}$ or $\frac{1}{20}$ gram eq. ($H = 1$) of the caustic or carbonated alkaline earths, the necessity of a calculation of the results is altogether dispensed with; in the former case the number of c.c., in the latter half the number of c.c. of the normal acid used, expresses the percentage required.

If we have to determine volumetrically the alkaline earths in soluble neutral salts of the latter, solutions which contain baryta, strontia, or lime salts are precipitated with carbonate of ammonia and ammonia, warmed, filtered, washed with pure water, and the precipitate then treated as described above. Magnesia salts may be precipitated by potash or soda solution, and the washed hydrate of magnesia treated in a similar manner, but in this case the result will be rather too low in consequence of the solubility of hydrate of magnesia.

4. THE MOST IMPORTANT TECHNICAL POTASH COMPOUNDS.

A. Potash or Pearlash.

§ 224.

Potash, which was formerly prepared almost exclusively from wood ashes, or from the ashes of other portions of plants, is now manufactured in large quantities, in the same manner as soda, by LEBLANC's process, that is, fusing sulphate of potassa with coal and carbonate of lime; potash is also obtained from the residues of beet-root molasses by evaporating them, calcining, lixiviating, and concentrating the liquor. In consequence of this, the substances contained in potashes, in addition to carbonate of potassa, may be very various. The following are specially to be noted, being *soluble in water*:—Sulphate of potassa, chloride of potassium, and carbonate of soda (generally only in small quantities in pearlash from the ashes of plants, but in considerable quantity in pearlash made by LEBLANC's method or from beet-root molasses). In smaller quantity there may or may not be found caustic alkalies, alkaline silicate, phosphate, and manganate, alkaline sulphides, and, by the action of the air on these, alkaline hyposulphites, besides alkaline cyanides and sulphocyanates; and, under certain circumstances, alkaline iodides and bromides and organic matter.

Of the constituents *insoluble in water* the following are to be specially noted :—Silica, silicate, carbonate and phosphate of lime, carbonate and phosphate of magnesia, oxide of iron, oxides of manganese, oxide of copper, alumina, sand, and coal.

Besides these ingredients, potashes as a rule contain water also.

The constituents insoluble in water can, as a natural consequence, easily be removed by treatment with water and filtration; but the frequent occurrence of carbonate of soda in the potash now found in commerce renders more difficult the analysis and determination of the ingredients soluble in water, as this substance particularly affects the amount of carbonate of potassa (or caustic potassa). It is necessary, therefore, before beginning the quantitative analysis of a potash, first of all to ascertain whether it contains an appreciable quantity of soda.

As potash absorbs water very rapidly, it is only possible to be sure of obtaining accurate and, on repeating the analysis, concordant results if in all the determinations of potash referred to an allowance is made for the amount of water originally present. Before opening the bottle, therefore, which contains the potash which is to be examined, two or three perfectly dry, well-stoppered test-tubes must be provided; these must be quickly filled after opening the bottle, stoppered, and kept under the desiccator.

I. Determination of Moisture.

About 2 grams of the potash is weighed off from one of the test-tubes into a platinum crucible, heated to dull redness, and the loss of weight determined; this is considered as water. The determination is not quite accurate if the potash contains free silica, as, on heating, this expels carbonic acid from the carbonate of potassa. In this case, if the moisture determination is to be accurate, it must be done according to § 36. If the potash contains hydrate of potassa, this water of hydration will not be driven off by ignition.

II. Determination of all the other Constituents.

a. About 10 grams of the potash is weighed from one of the test-tubes, treated with water in a beaker at a gentle heat until all the soluble portion is extracted, and the insoluble portion is filtered off on a small filter and washed with hot water until the washings no longer have an alkaline reaction. The filtrate and washings are collected in a 500 c.c. flask, and this is filled up to the mark with water. The filter with the insoluble residue is dried, ignited, treated with a little solution of carbonate of ammonia, again dried, gently ignited, and weighed. In almost all cases it is sufficient to enter the number thus obtained as "*portion insoluble in water.*"

b. 100 c.c. of the solution is treated according to § 220 or § 219. The acid required for neutralisation corresponds with the carbonate of potassa; also the hydrate of potassa, carbonate of soda, and hydrate of soda, if these are present. The amount of acid is first calculated for carbonate of potassa. If alkaline silicate is present in appreciable quantity, a correction must be made for it. Alkaline phosphates, sulphides, and cyanides also use up a portion of the acid; their quantity, as a rule, however, is so small that there is no need to make a correction for them.

c. 50 c.c. of the solution is carefully supersaturated with hydrochloric acid in a flask or covered beaker, heated to drive off the carbonic acid, and then evaporated to dryness in a porcelain or platinum dish; the residue is moistened with hydrochloric acid, extracted with water, and the silica filtered off and determined according to § 140, II. *a.* The filtrate is heated to boiling, and chloride of barium solution is cautiously added until it no longer causes a precipitate. The weight of the sulphate of baryta which is filtered off corresponds with the sulphuric acid present (§ 132, 1).

d. If the potash contains a determinable quantity of soda, the solution (in *c*) filtered from the sulphate of baryta is used for the preparation of the pure alkaline chlorides, and for the determination of the chloride of potassium contained in them. In this case it is evaporated to dryness, the residue extracted with water, and the excess of baryta is precipitated with carbonate of ammonia (§ 101, 2); the filtrate is then evaporated to dryness, the ammonia salt removed by gentle ignition, and the residue extracted with water; the last traces of baryta in the solution are removed by a little ammonia and carbonate of ammonia, the liquid filtered, evaporated in a weighed platinum dish, gently ignited, and the alkaline chlorides are weighed; the chloride of potassium contained in them is then determined as platino-chloride of potassium (this vol. p. 220), and the chloride of sodium is obtained by difference; from the latter, the soda contained in the potash can be calculated. It is obvious that the quantities of chloride of potassium and chloride of sodium in the weighed alkaline chlorides can also be determined indirectly (§ 152, 3), but this method can only be recommended when the quantity of soda salt present is not too small.

e. In 50 c.c. of the solution the chlorine is determined according to § 141, I. *a*, or *b*.

f. If the potash contains caustic alkali (that is, if its solution, after adding excess of chloride of barium, yields an alkaline filtrate), 200 c.c. of the solution is treated in a 500 c c. flask, with chloride of barium solution in excess; the flask is filled up to the mark with water, stoppered, shaken, allowed to settle, and the alkalinity determined in 250 c.c. of the clear fluid by means of normal acid (§ 222). The quantity used corresponds with the caustic alkali contained in 100 c.c. of the potash solution.

g. Lastly, smaller quantities of the potash solution are employed for qualitative tests for phosphoric acid, &c. If phosphoric acid is found in considerable quantity, as occasionally happens, it must of course be determined, and, since in that case the amount of carbonate of potassa cannot be accurately deduced from the determination of the alkalinity (II. *b*), a determination of the carbonic acid in the potash solution is necessary. For that purpose, the last 50 c.c. of the solution can be employed, and the determination made according to § 139, II. *d*, or *e*.

Calculation and Statement of Results.

Although a potash neither loses nor gains in value, if the bases and acids contained in it are combined as salts in one way or in another, yet it is very advisable that certain principles should be agreed upon in considering the arrangement of the results, as otherwise different chemists would calculate very different constituents of the potash from exactly the same analytical results. The author considers that it is the best way to combine any soda which may be present—if caustic alkali is present—first with water as hydrate of soda, then with silica as silicate of soda, then with carbonic acid as carbonate of soda. Potassa, on the other hand, should be returned first in combination with sulphuric acid, then (as potassium) with chlorine, then with carbonic acid, and silica, and lastly with water as hydrate of potassa.

In order to arrive at the exact quantity of carbonate of potassa—in the absence of determinable quantities of phosphoric acid—the following are to be subtracted, according to circumstances, from the number found in II. *b*, for carbonate of potassa.

1 eq. of carbonate of potassa for 1 eq. of hydrate of soda or potassa.
1 eq. of carbonate of potassa for 1 eq. of silicate of soda or potassa (NaO,SiO_2 or KO,SiO_2).
1 eq. of carbonate of potassa for 1 eq. of carbonate of soda.

If determinable quantities of phosphoric acid are present, the amount of alkaline carbonates must be calculated from the carbonic acid found.

III. Determination of the Amount of Potash only.

By the contents of a potash are properly understood the amount of carbonate of potassa contained in it, corresponding with the amount of carbonate and hydrate of potassa present.

If a potash contains no soda salt, the following methods are adapted for determining its composition; but *if a soda salt is present*, then the method of analysis described in II. will have to be employed, from which, according to circumstances, the determination of chlorine, sulphuric acid, and caustic alkali may be omitted.

1. About 10 grams of the potash is weighed out, dissolved in warm water, the solution filtered, and the residue washed; the filtrate and washings are then made up to 500 c.c., and the alkalinity is determined in 100 c.c. of this liquor by § 220, or in 200 c.c. by § 219. The amount of carbonate of potassa is calculated from the acid required for neutralisation. It is obvious that by this method not only the carbonate and caustic alkali, but also the silicate and phosphate of potassa, as well as any sulphide of potassium that may be present, are calculated as carbonate, and therefore cause a small error in the "contents," as defined above. For many uses of potash, however, the word error does not apply; for example, in making caustic liquor from potash by boiling its solution with hydrate of lime, as then the potassa, in combination with silicic and phosphoric acids, is also converted into caustic potash.

2. The carbonic acid is determined in about 5 grams of potash by § 221, and calculated in the contents as carbonate of potassa. If the potash contains carbonates of the alkaline earths, it is dissolved in water, filtered, and the concentrated filtrate is treated as directed. In presence of caustic potassa and sulphide of potassium, the process is conducted as with soda under similar circumstances (§ 229).

It is obvious from what has been stated in III. 1, that with potash containing silicate of potassa, phosphate of potassa, or sulphide of potassium, the results obtained by III. 1 and 2 cannot agree accurately.

If it is required not merely to know the total contents, but to form a more complete decision as to whether the contents is lowered by water, or by the foreign salts mixed with the carbonate of potassa in the potash, the alkalimetric estimation must be supplemented by a water determination (§ 224, I.). Guaranteed contents are always stated on anhydrous potash.

B. Chloride of potassium; and C. Sulphate of potassa.

§ 225.

Large quantities of potash salts, especially chloride of potassium and sulphate of potassa in various stages of purity, are prepared for different technical and agricultural purposes from the residual salts obtained in working the Stassfurt and other salt beds.

As a rule, the portion of these salts soluble in water contains the following bases: Potassa, soda magnesia, and lime, the acids being sulphuric and hydrochloric (that is, chlorine in the form of metallic chlorides). The residue insoluble in water consists chiefly of sand, clay, hydrated oxide of iron, and magnesia. Lastly, the salts always contain water; if chloride of magnesium is present in them, they are hygroscopic. The tests employed for these are almost exactly the same as those given for potash (this vol. p. 214).

I. Determination of Moisture.

A preliminary experiment determines the method by which the water determination has to be made; this consists in heating a sample of the salt in a glass tube, and examining whether the steam and condensed water have an acid reaction or not. The former is the case, for instance, if the salt contains chloride of magnesium. If the vapours are not acid, a water determination is made by gently igniting a sample of 1 or 2 grams in a platinum crucible; but if it has an acid reaction, this method yields too high a result. In that case 1 to 1·5 gram of the salt is weighed into a small boat, mixed with finely powdered, perfectly dry, carbonate of soda, and covered with a layer of the same; the boat is then pushed into a glass tube, about 200 mm. long, heated in a current of dry air, and the water given off is collected in a weighed chloride of calcium tube (§ 36).

II. Determination of all the Constituents.

a. About 10 grams of the substance is accurately weighed out, treated with warm water, and the insoluble residue filtered off and washed until the filtrate and washings amount to 500 c.c. The residue is dried, ignited, weighed, and its composition determined subsequently; it must be remembered, however, that it may still contain undissolved sulphate of lime.

b. The sulphuric acid is determined in 50 c.c. of the solution by § 132, I. 1, or 2, *e*.

c. The chlorine is determined in 50 c.c. by § 141, I. *a*, or *b*, *a*.

d. The lime is determined in 100 c.c. with chloride of ammonium, ammonia, and oxalate of ammonia, and the magnesia is precipitated from the filtrate as ammonio-phosphate of magnesia (§ 154, 6 *a*).

e. 50 c.c. of the solution is boiled with a little milk of lime to precipitate the magnesia, filtered, and washed. The filtrate is treated hot with chloride of barium until all the sulphuric acid is precipitated, and allowed to cool; ammonia and carbonate of ammonia are then added to precipitate the lime and baryta; the solution is filtered, evaporated to dryness, and the ammonium salts expelled by gentle ignition; the residue is treated with water, and the last portions of baryta and lime are precipitated by ammonia and carbonate of ammonia. The pure chlorides of the alkali metals are weighed, and the potash in them is determined (§ 224, II. *d*).

Calculation.

The inference that the sulphuric acid must be combined first with the lime and then with the magnesia, has been drawn from the order in which the salts separate, on evaporation, from solutions containing potash, soda, lime, magnesia, sulphuric acid, and hydrochloric acid.[*] The metals that are not present as sulphates, then appear in the total as metallic chlorides. After the chloride of potassium, the principal salts present are arranged in the following order:—CaO,SO_3—MgO,SO_3—$MgCl$—$NaCl$—KCl. This arrangement is moreover convenient, because it yields all the potassium as chloride of potassium, and consequently in the state of the salt which gives the material name and value. A different method of arrangement is chosen, as a rule, when sulphate of potassa is the most important salt present. According to this the sulphuric acid is combined, generally, first with lime, then with potassa, and, lastly, with magnesia, so that we obtain the following salts:—CaO,SO_3—KO,SO_3—MgO,SO_3—$MgCl$, and $NaCl$.[†] In favour of this way of arranging them, it may be urged that kieserite and chloride of potassium decompose into sulphate of potassa and magnesia, and chloride of magnesium. This method of arrangement has also the advantage that in stating the results the potash is all returned in the form of one salt.

III. Determination of the Total Potassium Present.

Frequently only one determination is desired for potash salts—namely, an estimation of the potassium, which, according to circumstances, is there calculated as chloride of potassium or sulphate of potassa. Since such determinations occur very frequently in works which make or use potash salts, attempts have been made to precipitate the potassa as acid tartrate of potassa or as perchlorate of potassa, to separate as alum, &c., but all these methods have been abandoned, as they do not yield sufficiently accurate results; and now potassa, at least for sellers' analyses, is always determined as platinochloride of potassium.[‡] On this account the author considers it sufficient to mention the other methods merely, and give references as to where they are to be found.[§]

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[*] See A. FRANK in Wagner's Jahresb. Chem. Tech. 1875, p. 480.

[†] *Ibid.* p. 495.

[‡] *Ibid.* p. 484.

[§] MOHR, Zeitschr. f. anal. Chem. 1, 59; ESSELENS, *ibid.* 4, 215; T. BECKER, method of A. FRANK, *ibid.* 6, 257; BOLLEY, *ibid.* 8, 505; FLEISCHER, *ibid.* 9, 331; E. SALKOWSKI, *ibid.* 11, 474; SCHLOSING, *ibid.* 11, 193; KRAUT, *ibid.* 14, 152.

In the employment of the platinochloride method the following questions have to be considered:—

(1) Is it necessary to precipitate the sulphuric acid? (2) Is it necessary to remove the lime and magnesia, and, subsequently, the excess of baryta which has been added, before precipitating the potassa as platinochloride of potassium? and, lastly, (3) Which method of treating the platinochloride of potassium is most to be recommended?

The first question is answered in the negative by TESCHEMACHER and SMITH,* if, as in saltpetre, only a little sulphuric acid is present, and that is combined with alkalies or magnesia; but, in the analysis of chloride of potassium and sulphate of potassa, in which attention must always be paid to the presence of sulphate of lime, and occasionally to that of large quantities of other sulphates, it may be unreservedly answered in the affirmative, as also by STOHMANN,† and, when somewhat larger quantities of sulphate are present, by G. KRAUSE.‡ To the second question it may be replied, that a separation of the alkaline earths (by the method laid down in § 225, II., or by precipitation at a boiling temperature by sulphate of soda [STOHMANN]), is not requisite (STOHMANN, KRAUSE, R. FRESENIUS, and A. SOUCHAY),§ because the double salts which chloride of calcium, chloride of magnesium, and chloride of barium form with chloride of platinum, are soluble in alcohol, but that, if the alkaline earths have not been removed, it is necessary to be particularly careful that only perfectly pure platinochloride of potassium is weighed. The reply to the third question is, that the platinochloride of potassium is best weighed in the manner recommended by the author,‖ and weighed in a small dish, and not on a tared filter.

The operation is conducted in the following way:—About 10 grams of the potash salt to be examined is weighed out, about 300 c.c. of water added, and the mixture heated until all the soluble portion is dissolved, filtered, and 1 c.c. of hydrochloric acid added; it is then heated almost to boiling, and chloride of barium added, with great care, until all the sulphuric acid is precipitated; any great excess of chloride of barium must be avoided. After it has settled, the solution is filtered into a litre flask, and, when cold, it is filled with distilled water up to the mark, and agitated; 50 c.c. of the liquid is taken out with a pipette, evaporated down to about 15 c.c., in a porcelain basin, and a sufficient quantity of solution of pure bichloride of platinum, which should be as neutral as possible, is added to convert, with certainty, all the metallic chlorides into platinum double salts and to leave an excess of chloride of platinum. By far the easiest way to effect this is to employ a solution of chloride of platinum of known strength, and adding—if the above-mentioned quantities have been employed—a volume containing 1 gram of platinum.

The solutions are mixed by means of a small glass rod, and evaporated to a syrupy consistence on a water-bath, the water not being allowed to boil;¶ 80 per cent. alcohol is poured on the residue when cold, and the whole carefully mixed and allowed to remain for some time with frequent stirring; the dark brownish-yellow alcoholic solution is then poured through an unweighed paper filter, which must not be too large, and the residue in the porcelain dish washed several times with small quantities of alcohol, until the platinochloride of potassium seems pure; this is finally collected on the filter and washed thoroughly with small quantities of the same alcohol repeatedly sprinkled on. The filter is now dried at a gentle heat in the funnel, until all the alcohol is evaporated, the dry contents of the filter are carefully transferred, as far as possible, to a watch-glass, and the filter, to which some portions of the double salt still cling, is placed again in the funnel and the salt adhering dissolved by small quantities of boiling water. The yellow solution thus obtained is evaporated to dryness in a small weighed platinum dish over a water-bath, the bulk of the precipitate in the watch-glass is then transferred to the platinum dish, and the whole dried at 130° until the weight is constant, and then it is weighed. If it is thought desirable to ascertain whether the platinochloride of potassium, that has been weighed, is pure, the method described in this vol. p. 155, may be followed; it gives accurate results.

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* Zeitschr. f. anal. Chem. 8, 90.

† *Ibid.* 5, 306.

‡ *Ibid.* 14, 184.

§ *Ibid.* 16, 63.

‖ *Ibid.* 16, 63.

¶ ULEX, Zeitschr. f. anal. Chem. 17, 175, finds it advantageous, after the addition of the chloride of platinum, to add to the solution 1 to 5 c.c. of a 20 per cent. solution of glycerine to prevent the platinochloride of sodium from becoming too dry, as otherwise it might not be completely dissolved.

If there is any reason for believing that the double salt first precipitated is not perfectly pure, the first weighing can of course be omitted and the method of purification just referred to is at once adopted.

The platinochloride of potassium that has been weighed should dissolve completely in boiling water, and samples of the dilute solution must not yield precipitates either with sulphuric acid or—after precipitation of the platinum by sulphuretted hydrogen—with oxalate of ammonia or with ammonia and phosphate of soda.

D. Nitrate of Potash.

§ 226.

In the analysis of commercial nitrate of potash as brought into the market, it is necessary to consider whether we are dealing with crude saltpetre or with the very pure saltpetre employed in the manufacture of gunpowder. In the case of *crude saltpetre*, determinations of chlorine, sulphuric acid, nitric acid, lime, magnesia, potash, and soda, insoluble residue and water are required. The analysis presents no special difficulties, and can, as a rule, be conducted according to the method given in § 225. The determination of the nitric acid is most easily performed by Reich's method (Vol. I. p. 390, *a*, *β*). The determination of water is found by the loss of weight when the saltpetre is heated to fusion. If acid vapours are given off, a little dry neutral chromate of potash must be mixed with the sample. Of course, this method of determining the water is only available if the saltpetre is free from organic matter. If there are appreciable quantities of nitrite present, the nitrous acid is determined by § 131, 5.

The analysis of nearly pure saltpetre is more difficult, as it involves the determination of very small quantities of lime, magnesia, soda, and chlorine, which nevertheless are of considerable importance in deciding the quality of the saltpetre. The following methods are to be recommended for the analysis of these pure nitres :*—

1. Determination of Moisture.

This is done, as usual, by moderately heating a weighed sample in a platinum crucible. The heat can be gradually increased until the saltpetre just begins to melt. The loss of weight gives the amount of water. With reference to the extremely small traces of nitrate of lime, nitrate of magnesia, and organic substances which saltpetres fit for gunpowder contain, the error resulting from their decomposition has no perceptible influence on the result.

2. Determinations of the Residue insoluble in Water and of the Chlorine.

100 grams of the saltpetre is dissolved in hot water, the residue collected on a small filter that has been dried at 100°, washed, and then dried at 100° and weighed. If the residue is considerable, the filter and residue are dried at 120°.

The filter is acidified with pure nitric acid, treated with nitrate of silver, and gently heated for some time, excluding light. The precipitate of chloride of silver is collected on a small filter and determined in the ordinary way, either as chloride of silver or as metallic silver.

In the case of such small amounts of chlorine, MOHR's volumetric method does not yield satisfactory results, as it is necessary to employ about 400 c.c. of a concentrated solution of saltpetre.

3. Determination of Lime, Magnesia, and Soda.

100 grams of the saltpetre is dissolved, with the addition of about 1·5 grams of chloride of potassium (which serves to decompose the nitrate of soda), in about 100 c.c. of water, by heating in a platinum or porcelain dish, and the solution is poured, with continual stirring, into about 500 c.c. of pure 96 per cent. alcohol. After it has settled, the crystalline precipitate is collected on a well-washed vacuum filter and washed with alcohol, the vacuum being maintained during the washing.

The filtrate is freed from alcohol by distillation, the residue dissolved in a small quantity of water, and the solution again poured into alcohol. After filtering off and washing the residue with alcohol, the latter is again distilled off, the residue again dissolved in water, and the solution is again precipitated with alcohol. After the residue has been washed with alcohol, the filtrate is an alcoholic solution in which all the lime, magnesia, and soda are contained with so little potash salt that a separation of the potash and soda appears practicable. It is to be noted that this conclusion is only accurate if the saltpetre is free from sulphates, as these, if present, will cause sulphate of lime to separate on precipitation with alcohol.

As a rule, however, the solutions of such pure saltpetre remain perfectly clear when treated with chloride of barium, and consequently contain no appreciable quantity of sulphates.

After the alcohol has been removed by evaporation from the last-obtained alcoholic solution, the small saline residue is repeatedly evaporated with hydrochloric acid to convert it into metallic chlorides free from nitrates, and in the filtered solution the lime is precipitated by a few drops of solution of oxalate of ammonia, filtered, and then, from the filtrate, the magnesia is thrown down by a small quantity of pure phosphate of ammonia. The filtrate from this is then heated in a platinum dish to remove the ammonia, one or two drops of a solution of ferric chloride added, and the liquid neutralised with ammonia or carbonate of ammonia so that it has a very slight alkaline reaction; it is then heated, and the precipitate of basic phosphate of iron removed by filtration. The filtrate is evaporated to dryness, the ammonia salts driven off, and the chloride of potassium separated as platinochloride of potassium; the alcoholic filtrate from this is then evaporated to dryness, and the platinochloride of sodium, together with the excess of chloride of platinum, is decomposed by cautious heating in a stream of hydrogen. The chloride of sodium is then extracted with water, the solution evaporated to dryness, and the soda calculated from the residue which is weighed, after it has been tested to see that it is free from potassa, lime, and magnesia. A determination of the chloride of sodium from the difference between the alkaline chlorides and the chloride of potassium corresponding with the platinochloride of potassium would be less accurate. It is of course necessary that unusual care should be taken to ascertain that all the reagents employed are perfectly pure.

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* R. FRESENIUS, Zeitschr. f. anal. Chem. 15, 65.

As it is interesting to note how small the impurities are in saltpetres intended for making gunpowder, the author appends the results of an analysis made by himself:

Nitrate of potassa	99.8124
Nitrate of soda	0.0207
Nitrate of magnesia	0.0093
Nitrate of lime	0.0006
Chloride of sodium	0.0134
Insoluble residue	0.0210
Moisture	0.1226
	100.0000

APPENDIX TO NITRATE OF POTASSA.

E. Analysis of Gunpowder.*

§ 227.

Gunpowder, as is well known, consists of nitre, sulphur, and charcoal, and, in the ordinary condition, invariably contains a small quantity of moisture. The analysis is usually confined to the determination of the three constituents and the moisture, but not unfrequently the examination is extended to the nature of the charcoal, and the carbon, hydrogen, oxygen, and ash therein are estimated.

In the first place (1) a process will be given by which the several constituents may be determined in different portions of substance, and also a choice of methods for determining the individual constituents.

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* As regards the determination of the sp. gr. of gunpowder, the author refers to HEEREN's paper on the subject, in "Mittheilungen des Gewerbevereins für Hannover," 1856, 168—178; Polyt. Centralbl. 1856, 1118. This method is criticised by E. LUCK (Zeitschr. f. anal. Chem. 12, 183). For the estimation of the density of prismatic powder see also BOTHE (Zeitschr. f. anal. Chem. 14, 99).

(2) By Link's method in which all the constituents are determined in one and the same portion of powder.

It seems impossible to say definitely which of these methods is undoubtedly the best under all circumstances; the author, therefore, leaves it to the analyst to select for himself the methods which best suit his particular purpose.

I. Process, in which the several Constituents are determined in separate Portions of the Powder.

a. Determination of the Moisture.

From 2 to 3 grams of the substance (not reduced to powder) is weighed between two well-fitting watch-glasses, and dried in the desiccator, or, at a gentle heat not exceeding 60°, until the weight is constant. Or the substance may be weighed in a glass tube drawn out at one end and provided with an ignited plug of asbestos, and dried by the passing of a slow current of dry air over it; comp. p. 227.

b. Determination of the Nitre.

An accurately weighed quantity of the powder (about 5 grams) is placed on a filter, which has been previously moistened with water; the powder is then wetted with as much water as it will take up, and, after some time, small quantities of hot water are repeatedly poured on to it until the nitrate of potassa is completely extracted. The first portion of the solution which runs through is received in a small weighed platinum dish, the washings in a beaker or small flask. The contents of the platinum dish are then evaporated, adding the washings from time to time; and the residue is cautiously heated to incipient fusion, and weighed.* If the charcoal and sulphur are collected on a filter which has been dried at 100° and weighed, and the filter and its contents, after thoroughly washing and drying at 100°, is weighed, and the increase in weight of the filter + the moisture determined in *a* (and calculated with reference to the quantity of substance taken) is deducted from the powder employed, the difference gives the nitre again by way of control. But this method of control cannot be recommended, as it is not only troublesome but also inexact, since the drying of sulphur at 100° is attended with loss.

c. Determination of the Sulphur.

a. By conversion into Sulphuric Acid in the Wet Way.

aa. From 2 to 3 grams of the powder is oxidised with pure concentrated nitric acid and chlorate of potash, the latter being added in small portions, while the liquid is kept boiling gently. If the operation is continued long enough, it usually happens that both the charcoal and sulphur are fully oxidised, and a clear solution is finally obtained. The solution is evaporated with excess of pure hydrochloric acid on a water-bath to dryness, the residue moistened once more with hydrochloric acid, again evaporated, filtered, if undissolved charcoal should render it necessary, and the sulphuric acid determined according to § 132, I. 1. For the method of purifying the sulphate of baryta, see this vol. p. 154, 4.

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* The accuracy of the nitre estimation is affected by the fact that the large amount of water necessary for the extraction also dissolves appreciable quantities of organic matter from the charcoal (see Link's process, p. 226). The nitrate of potassa may also be estimated in an expeditious manner, and with sufficient accuracy for technical purposes, by means of a hydrometer, which is constructed to indicate the percentage of this ingredient when floated in water containing a certain proportion of gunpowder in solution. A method based upon the same principle, proposed by Uchatius, is given in the Wiener akad. Ber. X. 748; also Ann. d. Chem. und Pharm. 88, 395.

bb. About 1 gram of the powder is boiled in a small flask with a concentrated solution of pure permanganate of potash, and more of the latter is added from time to time, until the violet coloration is permanent. The whole of the sulphur and charcoal will now be oxidised to sulphuric and carbonic acids respectively. Pure hydrochloric acid is added, the mixture heated until the separated binoxide of manganese is dissolved and the chlorine is expelled; it is then diluted, and the sulphuric acid precipitated with chloride of barium, § 132, I. 1 (CLOËZ and GUIGNET*).

β. By conversion into Sulphuric Acid in the Dry Way.

1 part (about 1 to 1·5 gram) of the finely triturated powder is mixed with the same quantity of pure anhydrous carbonate of soda (free from sulphuric acid), and 1 part of pure nitrate of potassa and 6 parts of pure and dry chloride of sodium added; the materials must be mixed most intimately, and the mixture heated in a platinum crucible until the combustion is completed and the mass has become white. The residue is dissolved in water, the solution acidified with hydrochloric acid, evaporated repeatedly with hydrochloric acid until all the nitric acid is destroyed, and the sulphuric acid which has been formed by the oxidation of the sulphur is precipitated with chloride of barium, as above, *c*, *a*, *aa* (GAY-LUSSAC).

γ. By Extraction with Bisulphide of Carbon and weighing the Sulphur. See LINK's process (next page).

d. Determination of the Charcoal.

A weighed quantity of the powder is repeatedly digested with sulphide of ammonium until all the sulphur is dissolved, the charcoal is collected on a filter which has been dried at 100°, washed first with water containing sulphide of ammonium, and then with pure water, dried at 100°, and weighed.

The charcoal thus obtained must, under all circumstances, be tested for sulphur by one of the methods given under *c*, *a* or *β*, and if necessary, the sulphur which remains in it must be determined in an aliquot part. The charcoal may also be examined as regards its behaviour to potash solution (in which "red charcoal"† is partially soluble), and an aliquot part may be subjected to elementary analysis according to § 188. For this purpose a portion of the charcoal, dried at 100°, is taken and dried at 190° (WELTZIEN). If the charcoal, on this second drying, suffers loss of weight, the latter must be calculated into percents of the gunpowder, deducted from the charcoal, and added to the moisture.

The sulphur, moreover, cannot be completely extracted by bisulphide of carbon (comp. LINK's process). If it is desired to subject the charcoal itself to analysis, LINK's process is particularly to be recommended, as the charcoal is much less liable to be affected when this method is employed than when it is digested with sulphide of ammonium.

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* Compt. rend. 46, 1110; Journ. f. prakt. Chem. 75, 175.

† Incompletely carbonised wood.

II. Process in which all the Constituents of the Gunpowder are determined in one Portion (after LINK*).

A glass tube *a*, of 9 mm. bore and about 140 mm. long, is selected, and, at one-third of its length, it is drawn out to 2 mm. bore, and cut off, leaving about 50 mm. of the narrow part. At the junction of the wide and narrow parts, a loose plug of ignited asbestos, about 15 mm. long, is placed; after being thoroughly dried the tube is weighed, the wide part filled with powdered gunpowder (about 3 grams) and weighed again. This gives the weight of the powder accurately. A current of perfectly dry air is now passed through the tube until it ceases to lose weight (say for 10 hours); the loss indicates the amount of moisture in the powdered gunpowder.†

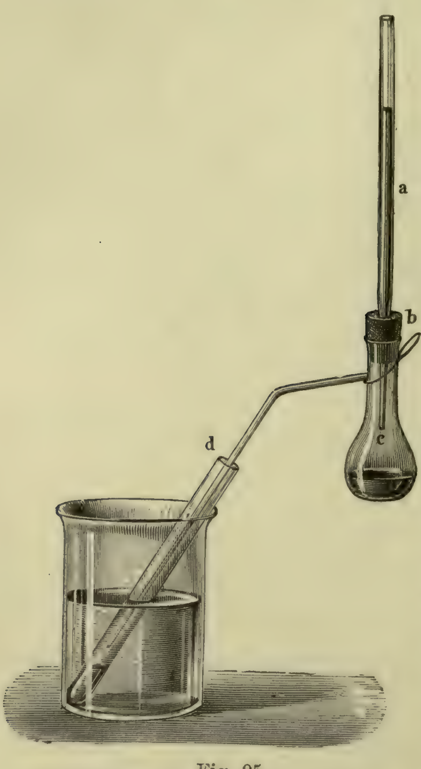

Fig. 95.

The tube *a*, fig. 95, is now connected by means of the cork *b* with the weighed flask, *c*, which should have a capacity of about 24 c.c., and the powder is treated with carefully rectified bisulphide of carbon, which will run through clear and rapidly into *c*. As soon as the little flask becomes, by repetition of this washing, about one-third full, it is heated by means of a water bath to a temperature of 70° to 80° and the bisulphide distilled into the *dry* receiver *d*. The distillate serves for repeating the extraction. After 8 c.c. of the liquid has been poured on the powder six times, all the sulphur that can be extracted will have been removed. The sulphur in *c* is cautiously heated just to fusion, the flask allowed to cool, and any vapour of bisulphide of carbon that may remain in it is removed by a stream of dry air: the flask is then weighed.

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* Annal. d. Chem. u. Pharm. 109, 53.

† This quantity is frequently somewhat greater than that contained in the gunpowder in its granulated condition, as it is very possible that the powder may attract a little moisture on trituration. On this account a correction must here be applied; see p. 228.

The tube containing the exhausted powder is again connected with the aspirator, and dry air is drawn through it at 100° until the weight remains constant. The difference between this weight and the original weight of the tube containing the dry, unexhausted powder represents the amount of sulphur extracted, together with the very small quantity of water which the powder, dried at the ordinary temperature, gives up when heated at 100°. This small quantity of moisture is found by deducting from the said difference the amount of the sulphur found directly. It must be added to the moisture found at first.

In order to determine the small quantity of sulphur still contained in the exhausted powder, a portion of the latter (0·5 to 0·7 gram) is shaken out, the tube weighed again, and in this way the quantity that has been taken out is known, as well as that which remains. The portion removed is oxidised with aqua regia, evaporated with hydrochloric acid, and precipitated with chloride of barium (comp. 1, *c*, *a*, *aa*); the sulphate of baryta is calculated into sulphur, and, from the latter, the quantity that would have been yielded by the whole of the exhausted powder can be ascertained. The amount thus obtained (which, according to LINK, will be about 0·1 per cent.) is added to the sulphur directly weighed.

The portion of exhausted powder remaining in the tube is now subjected to the following process for the determination of the nitrate of potassium. For this purpose, the tube *a* (fig. 96), together with the vessel *d*, is fastened air-tight to the air-pump receiver *b*, by means of the caoutchouc connector *e*. The contents of *a* are treated with cold water, and the machine worked very slowly so as to cause the liquid to pass, drop by drop, into *c*. In order to avoid crystallization of the salt at the point of the tube, this operation is repeated with warmer and warmer water, the water used at the end being as hot as possible—the vessel *d* being filled during the process with water which corresponds in temperature with that used for the exhaustion. In this way 2 grams of powder may be perfectly freed from nitre with 18 to 24 c.c. water, and, consequently, the error avoided which is caused by the use of large quantities of water, as this is liable

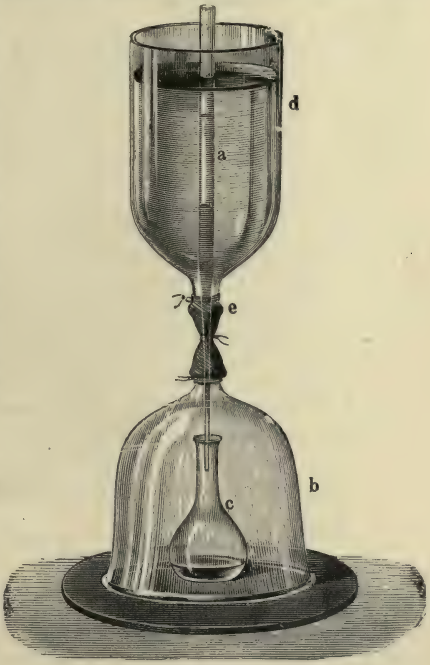

Fig. 96.

to take up an appreciable amount of organic matter from the charcoal.

The solution of nitre is evaporated to dryness in a platinum crucible, the residue dried at 120°, weighed, and calculated with reference to the whole of the powder.

The asbestos plug is now raised a little with a platinum wire, so as to loosen it, and the residual charcoal dried at 100° in a stream of dry air. If the weight of the charcoal is a little more than the weight of the nitre together with the charcoal *minus* the nitre found directly, this difference is occasioned by the fact that pure charcoal retains water more firmly than when it is mixed with nitre. The small difference in question (·001—·0015 gram) must, therefore, be considered as water adhering to the charcoal, and is to be deducted from the water obtained in the elementary analysis.

For the purpose of combustion, the charcoal is mixed in the tube with some chromate of lead, the drawn-out part is cut off, and the asbestos is mixed up with the contents, until a current of air can freely pass over the mass; the whole is then inserted into a combustion-tube filled in the proper manner with oxidised copper turnings, and burned as usual in a current of oxygen (§ 178). The quantities of carbon, hydrogen, and oxygen obtained (including the small quantity of ash) are also, like the nitre, to be calculated with reference to the whole quantity of powder originally taken.

If it is desired to correct the very small error which arises from the fact that powder attracts a little moisture on trituration, a fresh portion of the untriturated powder is dried in the manner described above, and, by the help of the number thus obtained, the weight of the original gunpowder contained in triturated powder can be calculated. Suppose the original granulated powder yielded 0·5 water, and contained, therefore, 99·5 dry powder, the weight of the dried triturated powder will have to be increased in the proportion of 99·5 : 100; this will give the quantity of granulated powder equivalent to it, that is, the true weight of the gunpowder employed.

F. Acid Tartrate of Potash (Tartar).

§ 228.

Crude tartar, which is partly taken from the wine vats and partly obtained from wine lees and serves for the preparation of tartaric acid and pure tartrates, almost always contains both tartrate of potash, $KO,HO,C_8H_4O_{10}$, and neutral tartrate of lime, $2CaO,C_8H_4O_{10} + 8Aq$, both in variable quantities, together with colouring matters, lees, &c. If gypsum has been used in the manufacture of the wine, as has been the practice for a long time, especially in France, the crude tartar will contain sulphate of lime.

In the examination of crude tartars, the question is either as to the total amount of tartaric acid they contain or how much of the tartaric acid is present in the form of tartrate of potash, and how much as tartrate of lime.

I. Determination of the total Tartaric Acid.

For this purpose M. **Léonard's** method, as briefly described by **Scheurer-Kestner**,* is the most convenient. It gives correct results, whether the tartar contains sulphate of lime or not.

About 5 grams of the tartar is dissolved in hydrochloric acid, filtered, neutralised with solution of caustic soda free from carbonic acid, and decomposed with an excess of chloride of calcium; after standing for some time, the precipitated tartrate of lime is collected, well washed, dried, ignited, and the residue titrated with normal hydrochloric or nitric acid (see § 223). Every 100 c.c. of the normal acid, required to neutralise the caustic lime or carbonate of lime resulting from the ignition of the tartrate of lime, represents 6·6 grams of anhydrous tartaric acid, $C_8H_4O_{10}$.

II. Determination of Acid Tartrate of Potash.

a. The determination of the acid tartrate of potash in crude tartar is, as a rule effected by neutralisation with normal soda solution strictly according to the method described, this vol. p. 196, 3. This determination, of course, is correct only if, in the tartar under examination, there are no other substances present (tannic acid, &c.), having an acid reaction, except the acid tartrate of potash.

b. If the method of determination described in *a* is not practicable, or is to be controlled, the following is to be recommended:—About 10 grams of the tartar is charred and heated with access of air for a sufficient length of time, but not too strongly, so that all the organic matter present may be completely decomposed. The residue is boiled with water, filtered, and washed with boiling water until the washings no longer have an alkaline reaction; the liquid, when cold, is made up to 500 c.c., and the potash (carbonate of potash and hydrate of potash) is determined in 200 c.c. by means of normal acid (§ 220)—100 c.c. of it is acidified with hydrochloric acid, chloride of barium is added, and, in the event of a precipitate occurring, the amount of the sulphate of baryta is determined. By calculating the ratio of the solution employed to the whole solution the following considerations lead to the desired result. If there is no sulphuric acid, the normal acid used is directly proportional to the carbonate of potassa formed from the acid tartrate of potassa, therefore 100 c.c. of normal acid must be calculated at 18·813 grams of acid tartrate of potassa, containing 13·2 grams of tartaric acid; if, however, sulphuric acid is present—that is, sulphate of potassa—this has been formed by the action of the sulphate of lime on carbonate of potassa, and, consequently, the quantity of acid tartrate of potassa cannot be directly deduced from the carbonate of potassa found (**Scheurer-Kestner**, *loc. cit.*); but it is correct, if for every 40 milligrammes of sulphuric acid present in the 500 c.c. of the alkaline solution, 1 c.c. of normal acid is added to the quantity which was required to neutralise the carbonate of potassa and caustic potassa contained in the 500 c.c., and from the total cubic centimetres of normal acid thus obtained the amount of acid tartrate of potassa is calculated by the proportion of 100 c.c. : 18·813 grams.

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* Remarques sur l'essai des tartres bruts présentées à la Société industrielle de Mulhouse dans sa séance, du 24 Avril 1878; Compt. rend. 86, 1024; Zeitschr. f. anal. Chem. 18, 111

III. Determination of the Tartrate of Lime.

If a determination of this is attempted in the neutralised solution of tartar obtained in II. *a*, by filtering off the solution of neutral alkaline tartrate, and estimating the tartrate of lime in the insoluble residue, an incorrect result will be obtained even in the case of a tartar free from gypsum, because solutions of neutral alkaline tartrates dissolve tartrate of lime in appreciable quantity; if the tartar contained gypsum, however, the results would be far more incorrect, because neutral alkaline tartrates are decomposed by gypsum, with the formation of alkaline sulphates and tartrate of lime, which separates (SCHEURER-KESTNER, *loc. cit.*). The quantity of tartrate of lime must be determined, therefore, either by subtracting the tartaric acid present in the form of tartar (method II.) from the total amount of tartaric acid as determined by method § 228, I., calculating the tartrate of lime from the difference; or by calcining the residue insoluble in water (§ 228, II. *b*), which consists principally of carbon and carbonate of lime, until the carbon is burnt off; the lime or carbonate of lime contained in the residue being determined by means of normal acid (§ 223). If no sulphuric acid is found in § 228, II. *b*, the normal acid employed in the neutralisation of the lime gives at once the amount of tartrate of lime (100 c.c. of normal acid corresponds with 13 grams of crystallised tartrate of lime with 8 eq. of water, or 9·4 grams of the anhydrous salt, or 6·6 grams of tartaric acid combined with lime). If, on the other hand, the alkaline solution contains sulphuric acid, the quantity of normal acid which corresponds with this (1 c.c. of normal acid for 40 milligrammes of sulphuric acid) must first be subtracted from the normal acid used in the neutralisation of the lime before the tartrate of lime can be calculated; since for each eq. of sulphate of potassa formed by the decomposition of the sulphate of lime by the carbonate of potassa, 1 eq. of carbonate of lime would separate.

5. SODIUM COMPOUNDS.

A. Soda.

§ 229.

Soda, which is the name for the carbonate of soda manufactured on the large scale and which contains other salts in smaller or larger quantities, is brought into the market in the calcined as well as the crystallised condition. Soda was, until a few years ago, almost exclusively made by the Leblanc process (by melting together sulphate of soda, coal, and carbonate of lime, extracting the melt, &c.); but latterly large quantities have been manufactured by heating bicarbonate of soda which has been obtained by the action of carbonic acid on a solution of salt saturated with ammonia (so-called ammonia soda). The soda made by the latter method is for the most part very pure, and contains, as a rule, only a little chloride of sodium.

In commercial Leblanc soda, however, especially in the lower qualities, a far larger number of foreign salts, &c., are present, especially sulphate of soda, chloride of sodium, silicate of soda, aluminate of soda, hydrate of soda, and, not unfrequently, sulphide of sodium, sulphite of soda, and hyposulphite of soda. Cyanide of sodium is also frequently found, although usually only in traces; ferrocyanide and sulphocyanate of sodium are also occasionally present in small quantities; to these must be added, in many kinds of soda, constituents insoluble in water, such as clay, sand, coal, oxide of iron, carbonate of lime, &c. Finally, the black ash prepared by the Leblanc process contains not only all the before-mentioned constituents soluble in water, but also, in the portion insoluble in water, large quantities of sulphide of calcium, carbonate of lime and caustic lime, together with magnesia, sulphide of iron, silica, alumina, sand, and carbonaceous matter. Its examination presents considerable difficulties, especially as the analysis would not afford much information as to the nature of the melt, if, without taking into account the solubility of the individual substances, the proportion of their different ingredients were alone determined in the mass. In order that the analysis may be of use to the alkali manufacturers, a determination must be made of the constituents which pass into solution on extracting the black ash with water, and of those which remain undissolved.

In the following pages the analysis of black ash is first considered and then that of commercial soda.

I. Analysis of Black Ash.

1. If the examination is to be confined to the substances which pass into solution, 53·04 grams of the finely powdered black ash (corresponding with one equivalent of carbonate of soda) is transferred to a flask holding 1000 c.c., which is filled up to the neck with water at 45–50°,* well closed, and shaken violently and repeatedly. After some hours, when the liquid has cooled to the mean temperature, the flask is filled up to the mark with cold water, 15 c.c. of water added (to allow for the bulk of the insoluble residue), closed, shaken, and allowed to settle.

The solution generally contains carbonate of soda, together with hydrate of soda, sulphide of sodium, sulphite of soda, sulphate of soda, chloride of sodium, silicate of soda, and aluminate of soda.

It is frequently considered sufficient to determine, on the one hand, the sum of the soda compounds which neutralise acid (expressed in the equivalent quantity of carbonate of soda), and, on the other hand, the sum of the sulphur compounds which convert iodine into hydriodic acid.

In this case the following determinations will suffice :—

a. 50 c.c. of the clear lye (corresponding with 2·652 grams of substance) are taken out with a pipette and subjected to the alkalimetric test (§ 220). Now, as $2{\cdot}652 = \frac{1}{20}$ eq. carbonate of soda, it is only necessary to double the number of c.c. of acid used, in order to obtain the *soda which has neutralised the acid* expressed in per-cents. of carbonate of soda.

b. 50 c.c. of the solution is transferred to a flask, diluted with about 200 c.c. of water, and pure dilute acetic acid (best prepared from glacial acetic acid) cautiously added with constant stirring, until the liquid has very nearly lost its power of colouring turmeric paper brown. When the number of c.c. of the dilute acetic acid required for this purpose has been ascertained, a fresh quantity of 50 c.c. of the solution is taken, diluted in a large flask with about 200 c.c. of water, and the same amount of acetic acid as was required in the preliminary experiment is slowly and cautiously added by means of a funnel tube reaching to the bottom of the flask; the latter being gently agitated all the time. The solution now contains acetate and bicarbonate of soda; some thin starch paste is added, and then standard iodine solution (§ 146, Vol. I. p. 369) until the liquid is just blue. The iodine used represents the *combined* deoxidising effect of the *sulphide of sodium and the sulphite of soda.*

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* The lixiviation is usually conducted at this temperature in the alkali works.

If the nature of the compounds which neutralise the acid and which decolorise the iodine solution are to be determined, and the other substances which are present in the solution have to be estimated, the following additional determinations must be made:—

c. Chloride of barium solution is added to 100 c.c. of the solution in a 500 c.c. flask, as long as a precipitate forms; the flask is filled up to the mark with water, and closed; when it has settled, 250 c.c. of the clear liquid, corresponding to 2·652 grams of substance, is drawn off, and subjected to the alkalimetric test (§ 220). The number of c.c. of normal acid used, multiplied by 2, gives the quantity of caustic soda present, expressed in per-cents. of carbonate of soda. This number multiplied by 0·7549 gives the percentage of *hydrate of soda.*

d. 100 c.c. of the solution is mixed in a half-litre flask with solution of sulphate of zinc, to which solution of potash has been added until the precipitate first formed is redissolved. The zinc solution is added until a tolerably strong precipitate is formed, and consequently the whole of the sulphur present as sulphide of sodium is precipitated as hydrated sulphide of zinc. The flask is now filled up to the mark with water, closed, shaken, and allowed to settle; 250 c.c. of the clear liquid (corresponding with 2·652 grams of substance) is drawn off, acidified with pure acetic acid, starch paste added, and then standard iodine solution until blue. From the amount of iodine used, the amount of *sulphite of soda* (1 eq. iodine = 126·85 corresponds with 1 eq. $NaO,SO_2 = 63·04$) can be calculated, and from the difference between the iodine used here and in *b*, the amount of *sulphide of sodium* (1 eq. iodine = 126·85 corresponds to 1 eq. $NaS = 39·04$) may be ascertained.*

Instead of the alkaline solution of oxide of zinc, an alkaline solution of oxide of lead may be employed for the precipitation of the sulphur combined with sodium; it is easily obtained by mixing a solution of acetate of lead with caustic soda solution until the precipitate first formed is redissolved. It is necessary, however, to take especial care that the lead solution is added in slight excess only. The determination of the sulphur combined with sodium may be finally controlled by filtering off the sulphide of zinc, or sulphide of lead, and analysing it gravimetrically (§ 108 and § 116).

e. 100 c.c. of the solution is evaporated to dryness with the addition of pure nitrate of potash, heated just to fusion, to convert the sulphide of sodium and sulphite of soda into sulphate, the fused mass dissolved in water, filtered into a 100 c.c. flask or cylinder, and the *chlorine* determined in 50 c.c. (corresponding with 2·652 grams of black ash) as directed in § 141, *b*, *a*, and in the other 50 c.c. the *sulphuric acid* as directed in § 132. From the amount of the latter, the quantity which corresponds with the sulphur of the sulphide of sodium and of the sulphite of soda is deducted.

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* Hyposulphite of soda in presence of sulphide of sodium in crude lyes may be determined in exactly the same manner. The analysis of lyes obtained as bye-products in the alkali manufacture is more difficult, as they contain sulphite of soda and hyposulphite of soda, as well as sulphate, and generally sulphide of sodium. The determination of these various oxygen compounds of sulphur is best accomplished by indirect analysis. See J. GROSSMANN, Zeitschr. f. anal. Chem. 18, 79.

f. 100 c.c. is acidified with hydrochloric acid, evaporated to dryness, the *silicic acid* separated as directed in § 140, II. *a*, and the *alumina* in the filtrate determined according to § 105, *a*.

In the calculation and arrangement of the results, the silicic acid and the alumina should be combined with soda to NaO,SiO_2 and NaO,Al_2O_3 respectively. The soda of these compounds, and also of the hydrate of soda and the sulphide of sodium, must be calculated into the equivalent quantities of carbonate of soda, and their sum deducted from the percentage obtained in *a;* the remainder is the carbonate of soda actually present.

If it is desired simply to determine the sulphide of sodium in soda lyes, the following expeditious process given by LESTELLE[*] may be used:—The lye to be tested is mixed with ammonia, heated to boiling, and standard ammoniacal solution of silver added, drop by drop, until the whole of the sulphur is just precipitated. When the point approaches, a portion is filtered off and tested, and this is repeated until further addition of silver solution causes a slight turbidity only. If the silver solution contains 2·764 grams of pure silver, or 4·3537 of pure nitrate of silver, in the litre, each c.c. corresponds with 1 milligram of sulphide of sodium. VERSTRAET[†] uses an ammoniacal solution of copper oxide instead of ammoniacal silver solution.

2. If the residue insoluble in water is to be examined the following is the easiest and surest method.

a. About 10 grams of the powdered black ash is placed in a flask with water, heated almost to boiling, and hydrochloric acid added little by little with continuous heating until there is a considerable excess of it, and all the soluble portion is dissolved. After the heating has been continued until all the carbonic acid and sulphuretted hydrogen have been expelled, the solution is passed through a filter which has been dried at 100° and weighed, and collected in a 500 c.c. flask; the residue is then washed and dried at 100°. This gives the sand and carbon; after ignition, the weight gives the sand alone, and the difference is the amount of carbon.

The solution is made up to 500 c.c. and mixed.

b. 200 c.c. of the solution is evaporated to dryness on a water bath after the addition of a little nitric acid, the *silica* is separated as usual, and the oxide of iron and alumina then precipitated by ammonia (§ 161, 4); after weighing, they are fused with acid sulphate of potassa, the iron is determined volumetrically or gravimetrically in the solution of the fused product (§ 160, A, 2), and the alumina is found by difference. In the filtrate from the ammonia precipitate, *lime* and, if it is present, *magnesia* are determined (§ 154, 6).

c. In 200 c.c. of the solution, the soda is determined by the method given in this vol. p. 154, 4.

d. A fresh portion of 0·7 or 0·8 gram of the powdered black ash is employed for the determination of the carbonic acid, and of the sulphur present in the form of sulphide of calcium, sulphide of sodium, and sulphide of iron, also of that which is expelled as sulphuretted hydrogen by the action of the hydrochloric acid. For this purpose, the method indicated by the author a few years ago* is employed, and the apparatus, depicted in fig. 97 and to which reference has been made (Vol. I. pp. 283 and 503, 7), is used.

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[*] Zeitschr. f. anal. Chem. 2, 94.

[†] *Ibid.* 4, 216.

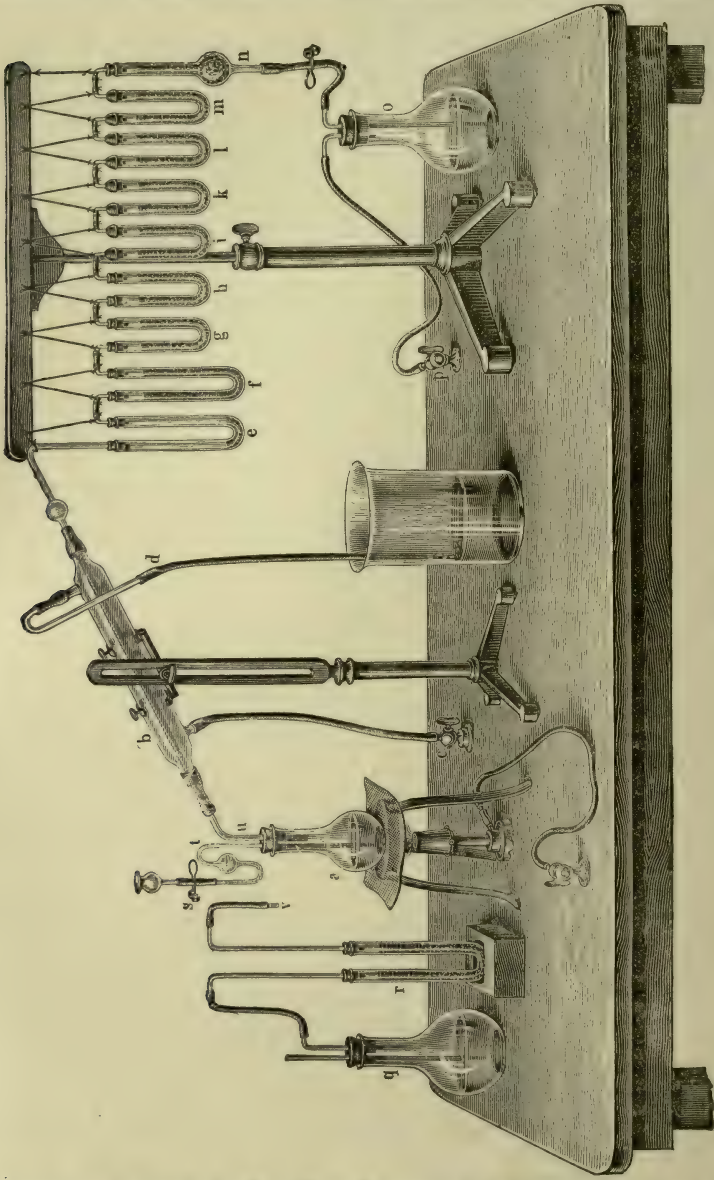

Fig. 97.

The flask *a*, which receives the weighed substance, holds about

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* Zeitschr. f. anal. Chem. 10, 75.

200 c.c. The tube *u*, which must not be too narrow, leads to the small reflux condenser *b*, the object of which is to condense the steam containing hydrochloric acid driven off during the latter portion of the heating. The small condenser is essential, as the heating must be continued for a long time in order to completely drive off the sulphuretted hydrogen. The condenser tube, which must not be too narrow, has a bulb near the top, and is connected with a U-tube *e*, which only contains a small quantity of chloride of calcium, and is empty at the upper part. Of the tubes which follow, *f*, *g*, and *h* contain chloride of calcium dried at 200°, *i* and *k* containing pumice stone, sulphate of copper, and chloride of calcium (see Vol. I. p. 383), *l* and *m* soda-lime and chloride of calcium; *i*, *k*, *l*, and *m* are accurately weighed; *n* contains soda-lime in the bulb and chloride of calcium in the tube and serves as a protecting tube; *o* is to be half filled with water and serves as an indicator of the progress of the operation; *p* is the suction tube of a water air-pump. Of course any other aspirator can be substituted for this.

The screw clamp *s*, on the funnel tube *t* that leads into the boiling flask *a*, is closed and the aspirator tap *p* is opened; in this way the apparatus can be tested as to whether it is tight in all its parts; for if so the air bubbles which at first pass through the water in *o* gradually cease.

If this is the case, the funnel over the clamp *s* is repeatedly filled with water, and this, by opening *s*, is allowed to flow into *a*, then hydrochloric acid of about 1·12 sp. gr. is introduced in the same way, in small portions, until there is a decided excess of acid. The liquid should occupy about one-third of *a*.

After the more rapid disengagement of gas has ceased, the little funnel over *s* is removed, and in its place the small glass tube *v* is fitted into the india-rubber tube above *s*, and the screw clamp is opened a little, so that a gentle stream of air may flow uninterruptedly through the liquid in *a*, and through the whole apparatus; the flask *a* is then heated, so that its contents are kept steadily and gently boiling. As soon as the water in the condenser begins to get warm, the tap *c*, in connection with the water supply, is opened sufficiently, so as to keep the condenser cool. The action of the sulphuretted hydrogen on the sulphate of copper pumice-stone is indicated by a progressive blackening, and that of the carbonic acid on the soda-lime by the progressive heating of the contents of the tube. After the contents of *a* have been gently boiling for about five minutes, the screw clamp is opened a little more, so that a somewhat stronger current of air is admitted, to completely remove the sulphuretted hydrogen and carbonic acid from the liquid, and carry them over into the absorption tubes. In order that the air introduced into the apparatus may be entirely free from carbonic acid, it is first passed through the potash solution contained in *q*, and then through the soda-lime tube *r*. An indication as to whether the sulphate of copper pumice and the soda-lime are sufficient for the amount of gas evolved, is afforded by observing whether the sulphate of copper pumice in the second absorption tube *k* is but little blackened, and the soda-lime in the second tube *m* is warmed but little.

After the stronger current of air has passed for fifteen minutes through the boiling liquid, the lamp under *a* is taken away, but the air is allowed to pass through the liquid for ten minutes more. The absorption tubes will now have become cold, and the operation is ended. The india-rubber tube is removed from *n*, *p* is closed, and the absorption tubes are removed and weighed. The increase of weight of the sulphate of copper tubes gives the amount of sulphuretted hydrogen, and that of the soda-lime tubes gives the carbonic acid. If the operation has been conducted as directed, the air in *a*, *e*, &c., has no longer any odour of sulphuretted hydrogen.

Calculation.

If, from the amounts of silica, alumina, soda, carbonic acid, and sulphur, which have been found in 2—viz., the total amounts in the black ash, the amounts found in 1—in the solution are subtracted, the results are the amounts of these substances remaining in the residue. In arranging the results, the iron is combined with sulphur as FeS, the remainder of the sulphur contained in the insoluble residue is combined with calcium as CaS, the carbonic acid in the residue is combined with lime, the remainder of the lime is reckoned as such, as also are the silica, alumina, and soda in the residue; it being difficult to determine in what combinations these substances exist in the residue.

The following ingredients are therefore determined in the solution and residue:—

Solution: NaO,CO_2,—NaO,HO,—NaO,SiO_2,—NaO,Al_2O_3,—NaS,—NaO,SO_3,—NaO,SO_2,—$NaCl$.

Residue: CaS,—CaO,CO_2,—CaO,—MgO,—FeS,—SiO_2,—Al_2O_3,—NaO,—Carbon,—Sand.

II. Commercial Soda.

Most soda comes into the market in the *calcined* condition, as "soda-ash," and a far smaller quantity in the crystallised state. The constituents of these have been considered above. With reference to the analysis of soda, especially soda-ash, the following points have to be considered:—

1. The collection of the sample for analysis and the determination of the water are performed exactly as in the case of potash (§ 224).

2. The determinations of all the other constituents present in appreciable quantity are carried out according to the methods recommended for the analysis of the substances which pass into the solution of the crude black ash (§ 229, I. 1).

3. If an insoluble residue remains on dissolving the soda in water, it is collected, washed, ignited, weighed, and eventually submitted to further analysis.

4. If the soda only is to be determined, the operation is conducted as in the case of potash determination, and the method adopted is generally § 224, III. 1, but occasionally § 224, III. 2.

In the former case the following is to be noted:—

If a soda contains sulphide of sodium, the errors that result from its presence can be avoided if the weighed sample of soda is ignited with chlorate of potassa before being neutralised. By this means the sulphide of sodium as well as the sulphite and hyposulphite of soda is converted into sulphate of soda. If hyposulphite of soda is present in any considerable quantity, this method is not available, as this salt, on being converted into sulphate of soda, decomposes an equivalent of carbonate of soda, and expels the carbonic acid.

$NaO,S_2O_2 + 4O$ (furnished by the chlorate of potassa) $+ NaO,CO_2 = 2(NaO,SO_3) + CO_2$.

If the determination of the amount of soda is performed according to § 224, III. 2, the following points must be carefully observed:—

If a soda contains *sulphide of sodium, sulphite or hyposulphite of soda, or chloride of sodium* in considerable quantity, the injurious influence of such compounds is counteracted as described in Vol. I. p. 338.

If the soda contains *caustic soda*, which may be known by the solution giving an alkaline reaction after addition of chloride of barium in excess, the carbonic acid will not give an indication of the amount of alkali present unless the hydrate of soda has been previously converted into carbonate. For this purpose about 5 grams of the soda (either dried or undried) is triturated in a mortar with 3 to 4 parts of pure quartz sand, and about ⅓ of powdered carbonate of ammonia, the mixture is transferred to a small iron dish, and the mortar rinsed with sand. The mass in the dish is moistened with as much water as it can absorb, allowed to remain for a short time, and then heated gently until the water is completely expelled; the residue is now quite free from any trace of carbonate of ammonia. If the soda under examination contains sulphide of sodium as well as caustic soda, the mass in the dish is moistened with solution of caustic ammonia instead of water, so as to reduce the sesquicarbonate of ammonia to neutral carbonate; otherwise sulphide of ammonium would be formed, and part of the sulphide of sodium converted into carbonate of soda.

When the mass is cold, it is transferred from the dish to the flask *A*, fig. 94, p. 203, which may be readily effected with the aid of a spatula, the dish rinsed with a little water, and the rest of the process conducted in the usual way, § 139. The addition of sand is intended to prevent the caking of the mass, and the spurting which would otherwise attend the expulsion of the water, unless the greatest caution were used in heating; moreover, the perfect removal of the dried mass from the dish would be rather difficult but for the sand. The latter operation (that is, the transfer of the mass from the dish to the flask) may be still further facilitated by coating the inside of the iron dish with fine sand before the introduction of the mixture; this is effected by moistening the inside of the dish with water, throwing sand into it, and shaking out the superfluous quantity.

If the soda contains silicate of soda and aluminate of soda, these will be converted into carbonate of soda by treatment with carbonate of ammonia.

Calculation and Arrangement of the Results.

Since the aqueous solution of commercial soda does not contain any other base except soda, there is no difficulty with regard to its calculation. Attention must be directed to one point, however. All soda is packed at the factories in the anhydrous condition. Its composition as guaranteed by the manufacturers is therefore based on its anhydrous condition. If the soda barrels are too long in stock, the soda frequently absorbs moisture; the barrels therefore become heavier, but the soda, when sampled and tested, indicates a smaller percentage of soda.

It is, therefore, advisable in analyses of soda always to calculate the contents in the anhydrous condition, and state the amount of moisture separately. If the amount of anhydrous soda corresponds with the guaranteed contents, and if the average amount of moisture (not that of a sample taken from the top) is in correct proportion to the increase in the weight of the barrel, then no objection can be made to the material.

In the soda trade, the amount contained is stated in degrees. As these degrees, however, have very different significations in different countries, the appreciation of the price of soda in various countries is, on this account, essentially difficult.

In Germany, a degree is equivalent to 1 per cent. of carbonate of soda ($NaO,CO_2 = 53{\cdot}04$); in France, the Gay-Lussac's degrees express the percentage of soda ($NaO = 31{\cdot}04$). English degrees represent the percentage of soda calculated by the equivalent of soda ($NaO = 32$, ratio between carbonate of soda and caustic soda as $53{\cdot}04 : 31{\cdot}43$), which was formerly considered correct, and is still retained, although it is now known to be false. Lastly, Decroizelle's degrees indicate how many parts by weight of hydrated sulphuric acid are neutralised by 100 parts of soda ($HO,SO_3 = 49$).

The different degrees, therefore, are in the following ratio:—53·04 German degrees are equal to 31·04 Gay-Lussac's, or 31·43 English, or 49 Decroizelle's degrees.

Whatever degrees may be used in stating the composition of the soda, one thing is certain, that in every case all the soda compounds that neutralise acids are calculated, according to circumstances, as carbonate of soda, soda, or soda capable of combining with sulphuric acid, that is, not only the carbonate of soda or caustic soda, but also the silicate of soda and aluminate of soda.

B. Common Salt

§ 230.

In commercial salt, the following ingredients are, as a rule, found in appreciable quantity:—

In the portion soluble in water:

Sodium, Magnesium, Calcium, Chlorine, Sulphuric Acid.

In the portion insoluble in water:

Carbonate of Lime, Silica, Clay, Oxide of Iron.

In small quantities are also found—

Potassium, Ammonium, Bromine, Organic Substances, &c.

With reference to taking the sample, the method mentioned for potash can be used (this vol. p. 215).

a. 10 grams of the powder is weighed out and dissolved in a beaker by digestion with water; the solution is filtered into a 500 c.c. flask, and the small residue which generally remains is thoroughly washed; finally the flask is filled up to the mark with water, and shaken.

If small white grains of sulphate of lime are left on dissolving the salt, they are reduced to powder in a mortar, water added, and the mixture allowed to digest for some time; the clear supernatant liquid is then decanted on to a filter, the undissolved deposit again triturated, water added, &c., and the operation repeated until everything is dissolved.

b. The dried insoluble residue from *a* is ignited and weighed, and

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then subjected to a qualitative examination, more especially with a view to ascertain whether it is quite free from sulphate of lime.

c. Of the solution *a*, the following quantities are measured off successively :—

For *d.* 50 c.c. corresponding with 1 gram of common salt
„ *e.* 150 c.c. „ „ 3 grams „ „
„ *f.* 150 c.c. „ „ 3 „ „ „
„ *g.* 50 c.c. „ „ 1 gram „ „

d. The *chlorine* is determined in the 50 c.c. measured off as directed in § 141, I. *a* or *b*.

e. The *sulphuric acid* is determined in the 150 c.c. measured off as directed in § 132, I. 1.

f. The *lime* and *magnesia* are determined in the 150 c.c. measured off as directed § 154, B. 6 (Vol. I. p. 421).

g. The 50 c.c. measured off is mixed in a platinum dish, with about 0·5 c.c. of pure concentrated sulphuric acid, and treated as directed in § 98, 1. The neutral residue contains the sulphates of soda, lime, and magnesia. From this, the quantity of the last two substances as ascertained from *f* is deducted ; the remainder is sulphate of *soda.*

h. The *water* is determined in another weighed portion of the salt, as directed in § 35, *a*, *a*, at the end.

i. If bromine, potassium, and other substances of which minute traces only are found in common salt, are present, they are estimated by the methods described in the analysis of mineral waters.

Calculation.

The sulphuric acid is taken first as combined with lime and then with magnesia. If there is still any sulphuric acid left, this may be combined first with potash, if this has been determined, and then with soda. If on the other hand there is a remainder of magnesia, it should be calculated as chloride of magnesium. This method of arrangement is in harmony with that adopted in the case of chloride of potassium (this vol. p. 219) and is based on the fact that if chloride of magnesium and sulphate of soda are dissolved in water and the solution is evaporated, chloride of sodium separates out. It may be remarked, however, that in the published analyses of salt, the manner in which the bases and acids are united as salts varies greatly.

C. Sulphate of Soda (Salt-cake).

§ 231.

The impure sulphate of soda formed in the salt-cake furnaces by the action of sulphuric acid on salt comes into the market under the name of salt-cake. It serves not only for the manufacture of soda, but is sent into the market, as such, in large quantity, as it is employed in glass manufacture. Smaller quantities are used for the preparation of crystallised Glauber's salt.

Salt-cake contains as a rule the following ingredients in appreciable quantities :—

Neutral sulphate of soda, also frequently some acid sulphate of soda, sulphate of iron, sulphate of alumina, sulphate of lime, sulphate of magnesia, chloride of sodium, and a residue insoluble in water.

The sampling is done as in the case of potash (this vol. p. 215).

1. *Determination of Moisture.*—If a sample, heated in a glass tube, gives off acid vapours, the loss of weight on ignition does not give the amount of water, but this must be determined as described in § 225, I.

2. About 10 grams of the sample is treated with about 100 c.c. of cold water, until the greater part of it is dissolved, it is filtered into a 500 c.c. measuring flask, and the residue is thoroughly washed with cold water. If the filtrate is cloudy, a little hydrochloric acid is added; the liquid is then made up to 500 c.c. and mixed.

3. The undissolved *residue* is ignited, weighed, and further examined according to circumstances. Care must be taken to ascertain whether it still contains sulphate of lime.

4. The sulphuric acid is determined in 50 c.c. of the solution (§ 132, I. 1, or 2, *e*).

5. 100 c.c. of the liquid, after the addition of chloride of ammonium, is heated with ammonia, and the oxide of iron, alumina, lime, and magnesia are determined according to § 229, I. 2, *b* (this vol. p. 233).

6. 50 c.c. is evaporated to dryness in a weighed platinum dish after the addition of 2 drops of pure concentrated sulphuric acid, ignited, finally in an atmosphere of carbonate of ammonia (§ 97, 1), and weighed. The residue gives the *soda* from the weight of the sulphate of soda, after the lime and magnesia have been subtracted as sulphates, and the iron and alumina as oxides. (This determination is not absolutely necessary if the method given in 8 is adopted, because the amount of soda may be calculated from the chlorine and sulphuric acid, but still it furnishes a good control.)

7. The chlorine is determined in 100 c.c. (§ 141, I. *a*, or *b*, *a*), provided hydrochloric acid has not been added in 2. If this has been done, a new portion of substance must be treated with water for the chlorine determination, and nitric acid added to the filtrate instead of hydrochloric acid.

8. Although the *acid sulphate of soda* present is already given by calculation—presupposing the determination of the soda—still it is important to make a direct determination. For this purpose about 5 grams of the sulphate are dissolved in the smallest possible quantity of cold water, about 9 grams of crystallised chloride of barium are added without filtering, then a small quantity of tincture of litmus, and finally, from a burette, $\frac{1}{10}$th normal soda solution until it shows the commencement of an alkaline reaction. If from the soda solution employed the equivalent quantity of sulphuric acid, corresponding with the sulphate of iron and alumina ($Fe_2O_3,3SO_3$ and $Al_2O_3,3SO_3$), is subtracted, the acid which is combined as hydrate with neutral sulphate of soda to form acid sulphate of soda ($NaO,SO_3 + HO,SO_3$), is obtained. With reference to the addition of chloride of barium see this vol. p. 201, *c*.

6. BARIUM COMPOUNDS.

Heavy Spar.

§ 232.

Heavy spar is employed partly as an adulterant of white lead, &c., partly for the production of chloride of barium and other preparations of baryta. If it is not pure white in the ground state, it is useless for the former purpose, and its purity is a criterion as to whether it will serve for the latter purpose.

Heavy spar must, therefore, frequently be submitted to chemical analysis. It contains, as a rule, besides sulphate of baryta, the following ingredients in appreciable quantity:—Sulphate of lime, sulphate of strontia, oxide of iron, alumina, silica, and moisture.

1. The *moisture* is determined most easily by gently igniting a sample of about 2 grams in a platinum crucible.

2. The portion left in 1, after ignition, is mixed with four times its bulk of carbonates of potash and soda, fused, and the product is treated with water (§ 132, II. *b*, *a*).

3. The solution obtained in 2 is carefully neutralised with hydrochloric acid, heated, to drive off the carbonic acid, evaporated to dryness, and the *silica* removed (§ 140, II. *a*); the *sulphuric acid* is determined in the filtrate (§ 132).

4. The residue from 2 is dissolved in dilute hydrochloric acid, evaporated to dryness, the product treated with hydrochloric acid, the *remainder of the silica* is removed (§ 140, II. *a*), and the oxide of iron and alumina are precipitated from the filtrate by ammonia (§ 161, 4). After a moderate washing, this precipitate is again dissolved in hydrochloric acid, heated, again precipitated by ammonia, collected, dried, ignited, and the *oxide of iron* and *alumina* determined by § 160, B, 12.

5. The filtrate obtained in 4, and which contains the alkaline earths, is neutralised with hydrochloric acid, heated, and dilute sulphuric acid added in slight excess; after the precipitate has completely settled, the supernatant liquid is poured through a filter (Filtrate I.). As soon as this is done, the bulk of the precipitate which has remained in the beaker, as well as that which has gone on to the filter, is treated, without previous washing, with carbonate of ammonia (§ 154, B, 3). The funnel containing the filter is closed at the end. After 12 hours it is opened, the liquid is allowed to run away, the contents of the beaker (Filtrate II.), together with the precipitate, are transferred to the filter, thoroughly washed, and treated with very dilute hydrochloric acid. The liquor which passes through is now mixed with filtrates I. and II., and the precipitate of now pure sulphate of baryta is dried and weighed, and the *baryta* is calculated.

6. The combined filtrates obtained in 5 are concentrated, care being taken that the liquid is just acid, 4 volumes of alcohol are added, and the whole is allowed to stand for 12 hours; the precipitate is then collected, washed with spirit, and finally the *strontia* and *lime* in the precipitate are separated by sulphate of ammonia (§ 154, B, 5).

7. Calcium Compounds.

A. Phosphate of Lime (Phosphorite, &c.)

(See V. Analysis of Manures.)

B. Chloride of Lime.

§ 233.

The "chloride of lime," or "bleaching powder" of commerce, contains hypochlorite of lime, chloride of calcium, and hydrate of lime. The last two ingredients are for the most part combined with one another as basic chloride of calcium. In freshly prepared and perfectly normal chloride of lime, the quantities of hypochlorite of lime and chloride of calcium present stand to each other in the proportion of their equivalents. When such chloride of lime is treated with dilute sulphuric acid, the whole of the chlorine it contains is liberated as "free" chlorine, as shown in the following equation:—

$$CaO,ClO + CaCl + 2(HO,SO_3) = 2(CaO,SO_3) + 2HO + 2Cl.$$

On keeping chloride of lime, however, the proportion between hypochlorite of lime and chloride of calcium gradually changes—the former decreases, while the latter increases. Hence from this cause alone, to say nothing of original difference, the commercial article is not of uniform quality, and on treatment with acid gives sometimes more and sometimes less chlorine. Now, as the value of this article, which is extensively manufactured and sold, depends entirely on the amount of chlorine set free on treatment with acid, it is very natural that chemists should endeavour to devise some simple method of determining the available amount of chlorine in any given sample of bleaching powder. The various methods proposed with the view of effecting this object have collectively received the name of Chlorimetry.

The number of chlorimetrical methods that have been proposed is so great, that all of them cannot be given here, but only a description of those which are distinguished either for the ease with which they may be carried out, or for the accuracy of the results.

Gay-Lussac's method, which depends on the conversion of arsenious acid into arsenic acid in a hydrochloric acid solution, and in which indigo solution serves as the indicator, was not considered in the Sixth Edition, because it is surpassed by Penot's method both in convenience and accuracy.

Before proceeding to describe the method, it may be noticed that the results obtained in testing chloride of lime are expressed in various ways. For while it is usual, scientifically, to define a chloride of lime according to the percentage of available chlorine it contains, as a rule the practice is to quote and sell it by chlorimetrical degrees. This method of expression, originated by Gay-Lussac, indicates how many litres of chlorine at 0° and 760 mm. pressure, are contained in 1000 grams of the chloride of lime.

These methods of expression may easily be deduced from one another, since we know that 1 litre of chlorine at 0° and 760 mm. weighs 3·1698 grams. Thus, for example, a chloride of lime of 90° would contain $3·1698 \times 90 = 285·282$ grams of chlorine in 1000 grams, and, therefore, 28·53 per cent., and a chloride of lime which contains 34·2 per cent. of chlorine is 107·9 degrees; for, since 100 grams contain 34·2 grams of chlorine, 1000 grams contain 342. These, however, $= \frac{342}{3·1698}$, that is $= 107·9$ litres.

Preparation of the Chloride of Lime Solution.

The solution is prepared for all the methods in the same way, and this is best done as follows:—

10 grams of the chloride of lime is weighed out, ground up finely with a little water, more water added gradually, and the mixture poured off into a litre flask; the residue is then ground up again with water, and

the contents of the mortar carefully rinsed into the flask; the latter is filled to the mark, the milky liquid shaken, and examined at once in that state, that is, without allowing it to settle; and every time, before measuring off a fresh portion, it must be shaken again. The results obtained with this turbid solution are much more constant and correct than when, as is usually recommended, the mixture is allowed to settle, and the determination is made with the supernatant clear portion alone. The truth of this may readily be proved by making two separate experiments, one with the decanted clear liquid, and the other with the residuary turbid mixture. Thus, for instance, in an experiment made in the author's own laboratory, the decanted clear liquid gave 22·6 per cent. of chlorine, the residuary mixture 25·0, the uniformly mixed turbid solution 24·5.

1 c.c. of the solution of chloride of lime prepared in this way corresponds with 0·01 gram of chloride of lime.

R. Wagner* recommends the preparation of the chloride of lime solution by shaking. He shakes together in a stout glass flask 10 grams of chloride of lime with coarsely powdered glass (pieces of broken-up glass rod about 5–10 mm. in length) and water, until the chloride of lime is completely divided. The volume of the pieces of glass is previously determined in a measuring cylinder in which the quantity of water poured on to it is measured. The milky liquid and the broken glass are rinsed into a litre flask, which is filled up to a litre at 17°·5, then a volume of water equal to the volume of the glass is added and the whole is shaken. One c.c. of this solution of chloride of lime corresponds, therefore, with 0·01 gram of chloride of lime.

A. Penot's Method.†

This method also, like the older one of Gay-Lussac, is based upon the conversion of arsenious acid into arsenic acid; but this conversion is effected in an alkaline solution. Iodide of potassium and starch paper are employed to ascertain the exact point when the reaction is completed.

a. Preparation of the Iodide of Potassium and Starch Paper.

The following method is preferable to the original one given by Penot:—3 grams of pure potato starch is stirred in 250 c.c. of cold water, boiled with stirring, a solution of 1 gram of iodide of potassium and 1 gram of crystallized carbonate of soda added, and the mixture diluted to 500 c.c. Strips of fine, white, unsized paper are moistened with this liquid, dried, and preserved in a closed bottle.

b. Preparation of the Solution of Arsenious Acid.

4·425 grams of pure arsenious acid‡ and 13 grams of pure crystallized carbonate of soda are dissolved in 600–700 c.c. of water, with the aid of heat. When the solution is cold, it is diluted to 1 litre. Each c.c. of this solution contains 0·004425 gram of arsenious acid, which corresponds with 1 c.c. of chlorine gas of 0° and 760 mm. atmospheric pressure.*

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* Zeitschr. f. anal. Chem. 4, 223.

† Bulletin de la Société Industrielle de Mulhouse, 1852, No. 118.—Dingl. polyt. Journ. 127, 134.

‡ The arsenious acid especially must be perfectly free from sulphide of arsenic, and the carbonate of soda from sulphide of sodium and sulphite and hyposulphite of soda, or else the solution will not remain unchanged. Whilst these compounds absorb oxygen in alkaline solution, they also allow the arsenious acid to gradually

c. The Process.

By means of a pipette, 50 c.c. of the solution of chloride of lime, prepared according to the directions of § 233, p. 242, is measured off and transferred to a beaker; the solution of arsenious acid, *b*, is added slowly from a 50 c.c. burette, with constant stirring, and at last drop by drop until a drop of the mixture no longer produces a blue spot on the iodised paper; it is very easy to hit the point exactly, as the gradually increasing faintness of the blue spots made on the paper by the liquid dropped on it, indicates the approaching termination of the reaction, and warns the operator to confine the further addition of the solution of arsenious acid to a single drop at a time. The number of ½ c.c. used indicates directly the number of chlorimetrical degrees (see note), that is, litres of chlorine gas in kilos. of "chloride of lime," as the following calculation shows: suppose 40 c.c. of solution of arsenious acid have been used, then the amount of chloride of lime employed in the experiment contains 40 c.c. of chlorine gas. Now, the 50 c.c. of solution employed corresponds with 0·5 gram of chloride of lime; therefore 0·5 gram of chloride of lime contains 40 c.c. of chlorine gas, and 1000 grams will contain 80,000 c.c. = 80 litres. This method gives very constant and accurate results, and appears to be particularly well suited for use in manufacturing establishments where there is no objection, on the score of danger, to the employment of arsenious acid.

B. MOHR'S Modification of PENOT'S Method.†

The principle of this modification is as follows :—A definite quantity of the chloride of lime solution is measured off, a measured quantity of a standardized solution of arsenite of potassa is added until it is in

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change into arsenic acid (F. MOHR, Lehrbuch der Titrirmethode, 5th ed. p. 321). In any case it is important to preserve the PENOT'S solution in small flasks with glass stoppers, completely filled, and to use a fresh flask for each set of experiments.

* PENOT gives the quantity of arsenious acid as 4·44 grams; but this number corrected in accordance with the now received equivalents of the substances and specific gravity of chlorine gas, is 4·425, as will be seen by the following proportion:—70·92 (2 eq. chlorine) : 99 (1 eq. AsO_3) : : 3·1698 (weight of 1 litre of chlorine gas) : x; $x = 4·425$, that is, the quantity of arsenious acid which 1 litre of chlorine gas converts into arsenic acid.

This solution is arranged to suit the foreign method of designating the strength of chloride of lime—viz., in chlorimetrical degrees (each degree represents 1 litre chlorine gas at 0° and 760 mm. pressure in a kilogram of the substance). This method was proposed by GAY-LUSSAC. The degrees may readily be converted into per-cents., and *vice versâ;* thus :—A sample of chloride of lime of 90° contains 90 × 3·1698 = 285·28 grams of chlorine in 1000 grams or 28·58 in 100, and a sample containing 34·2 per cent. chlorine is of 107·8°, for 100 grams of the substance contains 34·2 grams chlorine, ∴ 1000 grams of the substance contains 342 grams of chlorine; but 342 grams of chlorine = $\frac{342}{3·1698}$ litres = 107·8 litres, ∴ 1000 grams of the substance contains 107·8 litres of chlorine.

† Lehrbuch der Titrirmethode, 5th ed. p. 321.

excess, and the excess of the solution of arsenite of potassa that has been added is then determined with iodine solution (§ 127, 5).

Mohr employs:

A decinormal solution of arsenite of potassa and a corresponding decinormal solution of iodine. The former is prepared by digesting for a considerable time 4·95 grams (half of the tenth of an equivalent, because 1 eq. of AsO_3 is converted into AsO_5 by 2 eqs. of iodine) of pure powdered arsenious acid in a flask with 5 to 10 grams of bicarbonate of potassa and about 200 c.c. of water, shaking until the greater portion of the arsenious acid is dissolved. The clear liquid is then poured off into a litre flask, and the remainder of the arsenious acid is dissolved in water by the addition of small quantities of bicarbonate of potassa; 20 to 25 grams of bicarbonate of potassa are then added, and the whole is made up to 1 litre and shaken. 1 c.c. corresponds with 0·003546 gram of chlorine, therefore the arsenious acid contained in 1 c.c. is converted into arsenic acid by 0·003546 gram of chlorine.

The iodine solution is prepared by dissolving 6·4 grams of iodine in water by means of 9 grams of iodide of potassium, making up to 500 c.c.; the solution corresponds with that of the arsenious acid (§ 127, 5), and is diluted to agree with it.

In the valuation of chloride of lime, it is convenient to take 50 c.c. of the chloride of lime solution prepared according to the above instructions, to which solution of arsenite of potassa is added until a drop of the mixture no longer gives a blue spot on iodide of potassium and starch paper; it is then diluted with 150 to 200 c.c. of water, a solution of bicarbonate of ammonia prepared in the cold is added, then some starch solution, and lastly the iodine solution until the blue colour of the iodide of starch appears, and remains, even if a small quantity of solution of carbonate of ammonia is added. The cubic centimetres of iodine solution are subtracted from those of the arsenite of potassa solution, and in this way it is known how many cubic centimetres of the latter solution have been oxidised by the chloride of lime. These cubic centimetres, multiplied by 0·003546, give the amount of chlorine in 0·5 gram of the chloride of lime.

This method gives good results, but certainly does not supersede Penot's method, which is simpler in detail and quite as accurate.

C. Iodometric Methods.

In his treatise on "A Volumetric Method of very general applicability,"* Bunsen remarked that hypochlorites and especially chloride of lime could very well be analysed by decomposing the solution of the salt with iodide of potassium solution in excess, adding hydrochloric acid to feeble acid reaction and then determining the iodine volumetrically. For this purpose Bunsen employs, as is well known, an aqueous solution of sulphurous acid. Later, most chemists preferred hyposulphite of soda, as first proposed by H. Schwarz,† to an aqueous solution of sulphurous acid for the iodine determination, and it is in this way that the iodometric method which is described in § 146 originated. This "combined method" of iodine determination, which is so named elsewhere, has been especially recommended by R. WAGNER[*] for testing chloride of lime. F. MOHR[†] has declared WAGNER's method to be inaccurate; but C. WINKLER[‡] pointed out why MOHR had obtained varying results, and proved—as WAGNER had already done—that the method of iodometry, correctly carried out, also gives excellent results when hyphosulphite of soda is used. The author confirms this opinion, and advises the method to be carried out in the following manner:—

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* Annal. Chem. Pharm. 86, 277.

† Anleitung zu Maasanalysen, Supplement, Brunswick, Fr. Vieweg & Sohn, 1853, p. 21.

10 c.c. of the chloride of lime solution (containing 0·1 gram of chloride of lime) prepared according to the above directions, *b*, is placed in a beaker, about 100 c.c. of water added, and about 6 c.c. of the iodide of potassium solution (containing 0·6 of iodide of potassium) prepared according to Vol. I. p. 372, γ), the mixture is acidified with hydrochloric acid, and the iodine which separates is determined by § 146. Since 1 eq. iodine corresponds with 1 eq. chlorine, the calculation is easy.

R. WAGNER recommends using 2·5 grams of iodide of potassium for 1 gram of chloride of lime dissolved in 100 c.c. of water, and only allows the addition of hydrochloric acid to feeble acid reaction. An unnecessarily large excess of hydrochloric acid is not to be recommended, still there is no need to be very careful in acidifying. WINKLER (*loc. cit.*) obtained the equally good results, whether he added 1, 5, 10, or 20 c.c. of hydrochloric acid to 10 c.c. of chloride of lime solution after it had been decomposed with an equal quantity of iodide of potassium.

D. OTTO'S Method.

The principle of this method is the following:—

Two eq. of ferrous sulphate, when brought into contact with chlorine, in presence of water and free sulphuric acid, give 1 eq. of ferric sulphate and 1 eq. of HCl, the process consuming 1 eq. of chlorine.

$$2(FeO,SO_3) + HO,SO_3 + Cl = Fe_2O_3,3SO_3 + HCl.$$

Two eq. of $FeO,SO_3 = 152$, or of crystallised ferrous sulphate $2(FeO,SO_3,HO + 6aq.) = 278$, correspond with 35·46 of chlorine, or, in other terms, 0·7839 gram of crystallised ferrous sulphate corresponds with 0·1 gram of chlorine.

The ferrous sulphate required for these experiments is best prepared as follows:—

Iron nails, free from rust, are dissolved in dilute sulphuric acid, with the aid of heat in the last stage of the operation, and the solution is filtered, while still hot, into about twice its volume of spirit of wine; the precipitate consists of $FeO,SO_3 + HO + 6aq.$ This is collected upon a filter, washed with spirit of wine, spread upon a sheet of blotting paper, and dried in the air. When the mass no longer smells of spirit of wine, it is transferred to a bottle, which must be kept well corked.

The Process.

3·1356 grams (4 × 0·7839 gram) of the precipitated ferrous sulphate is dissolved in water, to 200 c.c., with the addition of a few drops of dilute sulphuric acid; 50 c.c., corresponding with 0·7839 gram of ferrous sulphate, is taken out with a pipette, diluted with 150 to 200 c.c. of water, a sufficiency of pure hydrochloric acid added, and the freshly shaken solution of chloride of lime, prepared according to § 225, is run in from a 50 c.c. burette, until the ferrous oxide is completely converted into ferric oxide. To know the exact point when the oxidation is completed, a number of drops of a solution of ferricyanide of potassium are placed on a plate; and, when the operation is drawing to an end, some of the mixture is added by means of a stirring rod to one of the drops on the plate, and notice taken whether it produces a blue precipitate; the experiment is repeated after every fresh addition of two drops of the solution of chloride of lime. When the mixture no longer produces a blue precipitate in the solution of ferricyanide of potassium on the plate, the number of volumes of the solution of chloride of lime employed is read off. The amount of solution of chloride of lime used contained 0·1 gram of chlorine.

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[*] Dingl. polyt. Journ. 154, p. 146; and 176, p. 131.

[†] Lehrbuch der Titrirmethode, 2nd ed. 1, 254; also Zeitschr. f. anal. Chem. 8, 311.

[‡] Dingl. polyt. Journ. 143, 198.

This method gives very satisfactory results, provided always that the ferrous sulphate is quite dry and free from ferric oxide.

Modifications of the preceding Method.

1. Instead of the solution of ferrous sulphate, a solution of ferrous chloride, prepared by dissolving pianoforte wire in hydrochloric acid (according to Vol. I. p. 218, β), may be used with the best results. If 0·6316 of pure metallic iron, that is, 0·6341 gram of fine pianoforte wire (which may be assumed to contain 99·6 per cent. of iron) is dissolved to 200 c.c., the solution will contain exactly the same amount of iron as the solution of ferrous sulphate above mentioned—that is to say, 50 c.c. of it corresponds with 0·1 gram of chlorine. But as it is inconvenient to weigh off a definite quantity of iron wire, it is better to weigh off, accurately, about 0·15 gram, dissolve it, dilute the solution to about 200 c.c., oxidize the iron with the solution of chloride of lime prepared according to the directions of § 225, and calculate the chlorine by the proportion

$$56 : 35{\cdot}46 :: \text{the quantity of iron used} : x;$$

the x found corresponds with the chlorine contained in the amount of the solution of chloride of lime used.

This method gives very good results. It has been described here principally because it dispenses altogether with the use of standard solutions. It is therefore particularly well adapted for occasional examinations of samples of chloride of lime, and also by way of control.

2. Instead of directly oxidising the ferrous oxide or chloride by the chloride of lime, the following may be employed:—About 0·3 gram of pianoforte wire is weighed off accurately, dissolved to ferrous chloride in a current of carbonic acid, and the strongly acid solution diluted to 200 or 300 c.c.; 50 c.c. of the solution of chloride of lime, prepared according to the directions of § 235, p. 242, is added slowly from a burette, the solution being stirred during the addition of the chloride of lime, and lastly, the quantity of iron which still remains unoxidized is determined by means of bichromate of potash (Vol. I. p. 220, *b*). (If permanganate is used instead of the bichromate, the remarks in Vol. I. p. 219, γ, must be borne in mind, as the solution contains hydrochloric acid.) By this means the quantity of iron which has been oxidized by the chloride of

lime is ascertained, and from this it is easy to calculate, by the formula given above, the percentage of chlorine contained in the sample.

There are other excellent chlorimetrical methods. For instance, a standard solution of ferrocyanide of potassium may be employed instead of a standard solution of a ferrous salt (E. DAVY*). The solution of chloride of lime is mixed with excess of ferrocyanide of potassium, the mixture is acidified with hydrochloric acid, and the unoxidised remainder of the ferrocyanide of potassium is determined with chromate of potassa. The reaction is complete when a drop taken out and mixed with dilute ferric chloride solution on a porcelain plate, is no longer coloured blue or green. The determination of the excess of ferrocyanide may be more conveniently made with a solution of permanganate (Vol. I. p. 378, *g*).

Again, the chloride of lime may be mixed with excess of solution of ferrous chloride, and the ferric chloride formed may be determined by means of stannous chloride (Vol. I. p. 225, *b*, *a*). Each eq. Fe_2Cl_3 corresponds with 1 eq. Cl ($2FeCl + Cl = Fe_2Cl_3$). The solution of iron employed must of course be free from ferric chloride, or, if it contains any, its quantity must be determined (comp. Vol. I. p. 394).

C. Acetate of Lime.

§ 234.

The acetates of lime, which are obtained by neutralising rectified or crude wood vinegar with hydrate of lime and evaporating the solutions, and which, as is well known, form the intermediate products between wood vinegar, and pure acetic acid or pure acetates, come into the market in bulk; and, as their composition is variable, they must always be tested for the amount of acetic acid they contain in order to fix their value.

The products consist of acetate of lime, with which small quantities of propionate and butyrate of lime, &c., are mixed, soluble compounds of empyreumatic substances with lime, and empyreumatic substances which remain undissolved on treatment with water; with these are generally associated small quantities of carbonate of lime, clay, &c. They also contain variable quantities of water.

In testing acetate of lime, the small quantities of propionic acid, butyric acid, &c., are, as a rule, determined with the acetic acid, and are calculated as such. If, under other circumstances, it must be treated so as to determine the amounts of these acids separately, the method proposed by E. LUCK † can be used.

Of the methods which are about to described, the first is suitable for acetates of lime of every description, but the two others are only for the purer varieties.

I. Distillation Method.‡

a. The weighed average sample (about 5 grams) of the acetate of lime to be tested is placed in a small tubulated retort, 50 c.c. of water and 50 c.c. of ordinary phosphoric acid (free from nitric acid) of about 1·2 sp. gr. is added, and the retort, with the neck inclined slightly upwards, is placed on a small sand-bath; the retort is connected with a small condenser by a glass tube bent at an obtuse angle, and the contents of the retort are distilled very nearly to dryness by gentle heating, care being taken that the distillate is collected without loss. A 250 c.c. measuring flask serves as receiver. It is better to surround the portion of the retort neck which is inclined upwards with a paper covering. When cold, the contents of the retort are diluted with 50 c.c. of water, and the liquid is again distilled nearly to dryness, the same operation being repeated a third time. The distillate is now diluted up to the mark, the mixture shaken, and the amount of free acid determined in 50 or 100 c.c. by means of normal soda solution (§ 215). Before the amount of acetic acid is calculated from the soda solution employed, a sample of the distillate is tested with silver nitrate. If there is only a slight opalescence, as is usually the case, the above calculation can be performed directly, that is, after calculating the relation of the portion taken to the whole: 6 grams of hydrated acetic acid or 7·9 grams of anhydrous acetate of lime correspond with every 100 c.c. of soda solution employed. If, on the other hand, the silver solution produces a considerable precipitate, insoluble in dilute nitric acid, the hydrochloric acid contained in the distillate must be determined in a proportional part, and be allowed for in the calculation.

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* Phil. Mag. (4) xxi. 214.

† Zeitschr. f. anal. Chem. 10, 184.

‡ R. FRESENIUS, Zeitschr. f. anal. Chem. 5, 315.

b. If acetates of lime have frequently to be tested by the distillation method, it is better to employ the steam distillation method proposed by the author.* The small tubulated retort is employed and arranged as in *a*, but it is better to have the condenser somewhat larger. A 500 c.c. measuring flask serves as receiver. A glass tube, bent at an oblique angle and slightly drawn out at the end inside the retort, dips into the tubulature of the retort. At the other end of the tube is a piece of india-rubber tube with a screw compression clamp; through this tube steam is passed as required.

For the supply of a current of a steam capable of being regulated exactly, a small iron or copper steam-boiler with a safety valve is the most suitable; if this is not obtainable, a flask fitted with an india-rubber cork, with two holes in it, is employed. A tube bent at right angles, and connected by a piece of india-rubber tubing with the glass tube which conveys the steam into the retort, is fitted into one of the holes; into the other is fitted one arm of a tube, bent twice at right angles, the other limb being about 250 mm. long. This dips into a stout test-tube, which is filled to the height of about 60 mm. with mercury; this test-tube, securely fixed in a large cork, stands in a beaker of cold water. It will be seen that the latter contrivance is to supply steam at a certain tension, and at the same time serves as a safety-valve, and allows the current of steam to be regulated at will.

Distillation is then carried on with the compression clamp closed, until there is only a small quantity of rather thick liquid remaining, and care is taken, by cautious heating, that the liquid, which is inclined to froth, does not come over. As soon as the contents of the retort again begin to froth, the heating of the small sand-bath is diminished, and, by carefully opening the screw clamp, steam, which, of course, must already have the required tension, is admitted. Distillation is proceeded with in this manner until the last drops which pass over have no longer any acid reaction. By more gently or more powerfully heating the sand-bath, and by opening the clamp more or less, the operation can be regulated at will, and be finished in a shorter time than is possible without the employment of steam.

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* Zeitschr. f. anal. Chem. 14, 172.

c. The distillation which is to be conducted according to *a* can also be accelerated by using diminished pressure. In this case, a distilling flask and a tubulated receiver of stout glass are employed, the latter being fitted air-tight to the condenser and through the tubulure—most conveniently by means of a water air-pump—air must be pumped out until the pressure on the liquid to be distilled is only about half an atmosphere. The distilling flask can be heated in a water-bath containing a saturated solution of salt; the air that is pumped out may be allowed to pass through a U-tube containing a small quantity of water. (See L. WEIGERT "On the Determination of Acetic Acid in Wine."*)

II. Alkalimetrical Method.

5 grams of the acetate of lime under examination is boiled with water, filtered into a 250 c.c. measuring flask, washed, and the filtrate when cold is made up to 250 c.c. and shaken; 100 c.c. is measured off, evaporated in a platinum dish, and the residue ignited with access of air until the carbon is burnt off; the amount of lime is then determined alkalimetrically (§ 223); 1 eq. of acetic acid is calculated for every eq. of lime thus found.

In the case of a salt considerably more contaminated with empyreumatic substances, this simple method of procedure yields, as already mentioned above, an incorrect (and indeed a too high) result, because the compounds of empyreumatic substances with lime dissolve in water in notable quantities along with the acetate of lime, and on evaporation and ignition likewise yield carbonate of lime or caustic lime.

III. Combined Acidimetric Method.

This method, published by the author a few years ago,† is based on the following reaction: If acetate of lime is treated with water until the soluble portion is dissolved, and oxalic acid in excess is added to the mixture, the precipitate contains all the lime as oxalate of lime, a portion of the empyreumatic substances, and also the clay, silica, sand, &c., whilst the substances with an acid reaction remain in solution, that is, the acetic acid, together with small quantities of its homologues and the excess of the oxalic acid used, namely, that portion which has not entered into combination with lime; there are, moreover, in the solution empyreumatic substances which have not an acid reaction, and which give the solution a more or less yellow or brown colour.

If then in the solution, on the one hand, a determination is made, by means of normal soda solution, of the acidity, that is, the sum of the acetic acid (together with propionic, butyric, &c., acids), and oxalic acid, and, on the other hand, of the amount of oxalic acid, it is only necessary to subtract the normal solution corresponding with the latter from the total quantity employed, in order to be able to calculate from the difference the amount of acetic acid (together with propionic acid, butyric acid, &c.) present.

This conclusion is, naturally, incorrect, if other neutral acetates are present in the acetate of lime whose bases are not precipitated as insoluble oxalates, or only incompletely, as, for instance, acetate of magnesia. But, as every maker of acetate of lime knows that the employment of lime containing magnesia for the saturation of wood vinegar diminishes the value of the product obtained, acetates of lime strongly contaminated with magnesia are rarely met with in commerce; it is seldom, therefore, that an error of any great importance arises from an acetate of lime containing acetate of magnesia; the effect, however, would be the subtraction of too large a quantity of oxalic acid, namely, the sum of the free and of the combined oxalic acid which remains in the solution, from the total of the free acids found, causing the amount of acetic acid found to be too low.

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* Zeitschr. f. anal. Chem. 18, 207.

† *Ibid.* 13, 153.

Method of procedure.—5 grams of the acetate of lime to be examined is accurately weighed out, and introduced into a 250 c.c. flask which also has a mark at which it holds 252·1 c.c.; it is then dissolved in about 150 c.c. of water, and to this, without filtering, 70 c.c. of normal oxalic acid solution is added, the flask is filled up to the 252·1 c.c. mark,* closed with an india-rubber cork and well shaken, the contents are allowed to settle, and filtered through a dry folded filter, using a covered funnel, into a dry flask until at least 200 c.c. of filtrate have been obtained.

1. 100 c.c. of the clear, usually yellow, filtrate is taken, a little tincture of litmus added, and then normal soda solution, until quite neutral. As the colour of the liquid interferes with observing the change of red to blue, litmus and turmeric papers must be employed to exactly fix the point of neutralisation; it is also advisable to determine it several times by adding, after the end of an experiment, a small measured quantity of normal hydrochloric acid and then normal soda again to saturation. The titration may be considered as finished as soon as concordant numbers are obtained in this manner. By multiplying the number of cubic centimetres of soda solution employed by 2·5, the amount corresponding with the 250 c.c. solution, that is, with the 5 grams of substance taken, is found.

2. A second 100 c.c. is taken, a solution of pure acetate of lime added, the mixture allowed to settle at a moderate heat, the oxalate of lime filtered off, washed thoroughly, and converted in the usual manner (by gentle ignition and treatment of the residue with carbonate of ammonia, &c.) into carbonate of lime; the number obtained is then multiplied by 50 (see below), and the number of cubic centimetres of soda solution which the free oxalic acid contained in the 250 c.c. solution required for saturation is thus found. This number of cubic centimetres of soda solution is subtracted from that found in 1, and from the remainder the acetic acid (together with the small quantities of propionic acid, butyric acid, &c.) contained in the 5 grams of substance is calculated.†

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* The 2·1 c.c. (that is the difference between 252·1 and 250 c.c.) represent—as far as this is possible without accurately knowing the composition of the acetate of lime—the space which the precipitated oxalate of lime (of which the sp. gr. is 2·2202) occupies.

† The abbreviation of the calculation, as contained in these instructions, namely, the fact that it is only necessary to multiply by 50 the weight of the carbonate of lime obtained from 100 c.c. of filtrate, by gentle ignition of the oxalate of lime, in order to find the number of cubic centimetres of normal soda solution which

If there is an objection to weighing the carbonate of lime obtained by gentle ignition of the oxalate of lime, the oxalate of lime obtained from 100 c.c. of the acid filtrate by precipitation with acetate of lime may be strongly ignited and the lime in the residue, whether it is contained in it as caustic lime or carbonate of lime, may be determined by titration with normal hydrochloric acid, titrating back the excess of the free hydrochloric acid by normal soda solution (§ 223.) The calculation is then simply effected by subtracting the number of cubic centimetres of normal hydrochloric acid required for the neutralisation of the lime obtained from the oxalate of lime from the number of cubic centimetres of normal soda solution required for neutralising the free acid in 100 c.c. of the filtrate. The remainder, multiplied by 2·5, gives then directly the amount of soda solution which corresponds with the acetic acid (together with propionic acid, butyric acid, &c.) contained in the 250 c.c. filtrate, and therefore in the substance weighed out.

The author found that the results obtained by this method corresponded very satisfactorily with those yielded by the distillation method in the case of acetate of lime prepared from rectified wood vinegar.

D. Analysis of Limestones, Dolomites, Marls, Cements, &c.

§ 235.

As the minerals containing carbonate of lime and carbonate of magnesia play a very important part in manufactures and agriculture, their analysis has often to be undertaken in a chemical laboratory. The analytical process differs according to the object in view. For technical purposes, it is sufficient to determine the principal constituents; the geologist takes an interest also in the substances present in smaller proportions; whilst the agricultural chemist seeks a knowledge not only of the constituents, but also as to the degree of solubility, in different menstrua, in which they are severally present.

In the first place, a process is given for a complete and accurate analysis; in the second place, the volumetric methods by which the carbonate of lime (and the carbonate of magnesia) may be determined; and, lastly, the analysis of the products formed by heating these minerals, that is, quicklime and cements.

An accurate qualitative examination should always precede the quantitative analysis.

I. Method of Complete Analysis.

a. Some large pieces of the mineral are reduced to powder, mixed uniformly, and placed in a well-closed bottle.

correspond with the free oxalic acid present in the 250 c.c. solution, is based on the following proportions from which the free oxalic acid contained in the 250 c.c. is calculated from the carbonate of lime ($=y$) obtained from the oxalate of lime from that in 100 c.c.:

$$100 : 250 :: y : x.$$

The carbonate of lime (y') thus found for the 250 c.c. is calculated into oxalic acid by the proportion

$$50 : 36 :: y' : x$$

and the oxalic acid thus found is calculated into normal soda solution by multiplication by $\frac{1000}{36}$; but $y \times \frac{2{\cdot}5 \times 36 \times 1000}{50 \times 36} = y \times 50$.

b. About 2 grams of the powdered mineral is weighed between two watch-glasses, and dried at 100° until the weight is constant (the loss of weight gives the moisture); the powder is then placed in a beaker, water is added, the mixture warmed, the beaker covered with a large watch-glass, and hydrochloric acid added gradually until the carbonates are just dissolved. The employment of a large excess of hydrochloric acid and strong heating should be avoided in order that the admixed clay may be decomposed as little as possible. After somewhat prolonged gentle heating, the residue remaining undissolved is collected on a filter paper previously dried at 100°, and weighed; the residue is then washed and weighed. It generally consists of separated *silicic acid, clay, and sand;* but it often contains also *humus-like matter.* Opportunity will be afforded in *g* for examining this residue.

c. The hydrochloric acid solution is mixed with chlorine water, then with ammonia in slight excess, and the whole allowed to remain at rest for some time, in a covered vessel, at a gentle heat; the precipitate is then collected. It contains—besides the hydrates of ferric oxide, sesquioxide of manganese, and hydrate of alumina—the silicic acid which may have passed into solution, phosphoric acid, and, moreover, invariably traces of lime and magnesia; it is washed slightly, and re-dissolved in hydrochloric acid; the solution is heated, chlorine water added, and it is then precipitated again with ammonia; the precipitate is collected on the same filter, washed, dried, ignited, and weighed.

In the case of dolomites, if a pure white precipitate (hydrate of magnesia) is obtained on the addition of ammonia, instead of a small yellowish one, the solution does not contain sufficient chloride of ammonium. In this case, the precipitate suspended in the liquid must be dissolved by means of hydrochloric acid, chlorine water added, and the solution again precipitated with ammonia.

For the estimation of the several components of the precipitate, namely, *ferric oxide, protosesquioxide of manganese, alumina,* and *phosphoric acid,* opportunity will be afforded in *g.*

d. The liquids filtered from the first and second precipitates produced by ammonia are mixed, and the *lime* and *magnesia* in them determined as directed in § 154, 6 (36).

e. As a rule, the minerals which are considered here contain, besides moisture, a small quantity of water which is not driven off on drying at 100°. For the determination of this, a fresh sample of the undried mineral, or of that which has been dried at 100°, is placed in a small boat, which is inserted in a glass tube about 250 mm. long, and heated in a stream of dry air, the water being collected in a weighed chloride of calcium tube (§ 36). As several minerals throw off dust when treated in this way, the glass tube is constricted in front of the boat and a loose plug of asbestos introduced there to retain the powder. The tubes, asbestos plug, and corks are thoroughly dried by heating in a current of air before the boat with the powdered mineral is introduced. If the substance dried at 100° has been employed, the increase in weight of the chloride of calcium tube gives directly the amount of combined water. When an undried mineral is used, the moisture determined by *a* must be subtracted from the total water contained in it, in order to find the amount of combined water.

f. If the limestone contains no other volatile constituents besides water and carbonic acid, it is ignited with fused borax (Vol. I. p. 336, *c*). If the material has been dried at 100°, the water found in *e* is subtracted from the loss of weight which it undergoes; the difference is the *carbonic acid;* if, however, the undried mineral has been employed in both, the combined water, *e*, and the moisture must be subtracted. If this method is inapplicable, the carbonic acid is determined as directed Vol. I. p. 338, *bb*, or, more accurately, by the method given Vol. I. p. 340.

g. To effect the estimation of the constituents present in smaller proportion, as well as the analysis of the residue insoluble in hydrochloric acid, and of the precipitate produced by ammonia, 10 to 50 grams of the undried mineral is dissolved in dilute hydrochloric acid in the manner described in *b* (above). The solution is gently heated for some time, to expel the carbonic acid, then filtered through a weighed filter into a litre flask, and the residue washed, dried, and weighed.

a. Analysis of the insoluble Residue.

aa. A portion is treated with boiling solution of pure carbonate of soda (§ 235, *b*), and the silicic acid separated from the solution (§ 140, II. *a*); in this way the amount of *silicic acid soluble in alkalies,* is ascertained.

bb. A portion is ignited with access of air; the loss of weight corresponds with the amount of water together with organic matter. The silica and bases are determined in the residue left on ignition (§ 140, II. *b*). The silica found in *aa* is subtracted from the quantity obtained here, and thus the silica present in the form of clay and sand is ascertained. If it is required, as in the determination of the constituents of hydraulic lime, to estimate both these separately, an additional portion of the residue must be heated with sulphuric or phosphoric acid. (See Analysis of Clay.)

cc. If the residue contains *organic matter* (humus) in somewhat considerable amount, a portion is submitted to ultimate analysis (this vol. p. 25). PETZHOLDT,* who determined by this method the colouring organic matter of several dolomites, assumes that 58 parts of carbon correspond with 100 parts of organic substance. Of the hydrogen found, 4·5 parts for every 58 of carbon are to be calculated as belonging to the organic matter, the remainder is to be reckoned as derived from water contained in the residue.

dd. If the residue contains *pyrites,*† another portion of it is fused with carbonate of soda and nitrate of potassa; the melt is macerated in water, hydrochloric acid added, the whole evaporated to dryness, the residue moistened with hydrochloric acid, gently heated with water, filtered, and the sulphuric acid determined in the filtrate; from the result the amount of pyrites present is calculated.‡

β. Analysis of the Hydrochloric Acid Solution.

aa. 500 c.c. of the hydrochloric acid solution that was made up to 1 litre is employed for the determination of the *silicic acid* that has passed into solution, and of the *baryta*, *strontia*, *alumina*, *manganese*, *iron*, and also traces of copper and other metals precipitated by sulphuretted hydrogen (this vol. p. 159, B).

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* Journ. f. prakt. Chem. 63, 194.

† Compare PETZHOLDT, *loc. cit.*; EBELMEN (Compt. rend. 33, 681); DEVILLE (*ibid.* 37, 1001; Journ. f. prakt. Chem. 62, 81); ROTH (Journ. f. prakt. Chem. 58, 84).

‡ If the residue contains sulphate of baryta or strontia, these compounds are formed again on evaporating the soaked mass with hydrochloric acid; they remain accordingly on the filter, whilst the sulphuric acid formed by the sulphur of the pyrites passes into the filtrate.

bb. The phosphoric acid is determined in 250 c.c. of the hydrochloric acid solution, according to this vol. p. 161, 7.

cc. The remaining quarter of the dilute hydrochloric acid solution is used for the estimation of the *alkalies.*[*] For this purpose, it is mixed with chlorine water, then with ammonia and carbonate of ammonia; after allowing the mixture to stand for some time, the precipitate is filtered off, the filtrate evaporated to dryness, the residue ignited in a platinum dish to remove the ammonia salts, and finally the magnesia is separated from the alkalies as directed in Vol. I. p. 415, β. In order that trustworthy results may be obtained, the reagents must be most carefully tested for fixed alkalies, and the use of glass and porcelain vessels avoided as far as practicable.

Should the limestone or dolomite contain a sulphate soluble in hydrochloric acid, the sulphuric acid is precipitated by a small excess of chloride of barium, allowed to settle, and the sulphate of baryta filtered off (this must be determined in the usual manner) before proceeding as above to the estimation of the alkalies.

h. The iron found in *g* may be present in the mineral as ferric oxide or ferrous oxide, or as compounds of both oxides. In order to decide this question, about 10 grams of the undried mineral is dissolved in a 250 c.c. measuring flask by warming with dilute hydrochloric acid. (Apparatus as in fig. 80, Vol. I. p. 216.) After the cooled solution has been diluted to 250 c.c. and shaken, it is allowed to settle, 100 c.c. of the liquid is taken out by means of a pipette, and the amount of ferrous oxide determined by PENNY's method (Vol. I. p. 220). The quantity contained in the mineral as ferric oxide is eventually determined by the difference.

i. As calcite and aragonite may contain *fluorides* (JENZSCH[†]), the possible presence of fluorine must not be disregarded in accurate analyses of limestones. A large sample of the mineral, therefore, is treated with acetic acid until the carbonate of lime and carbonate of magnesia are decomposed, the whole evaporated to dryness until the excess of acetic acid is completely expelled, and the residue extracted with water (§ 138, I.). The fluorine remains in the residue. If it can be distinctly detected in a portion of this,[‡] the determination may be attempted in the manner described, § 166, 4, *b*.

k. If the limestone under examination contains *chlorides*, a large sample is treated with water and nitric acid, at a very gentle heat, filtered, and the chlorine precipitated from the filtrate by solution of nitrate of silver.

l. It is often interesting for agriculturists to know the degree of solubility of a limestone or marl in the weaker solvents. This may be ascertained by treating the sample first with water, then with acetic acid, finally with hydrochloric acid, and examining each solution and the residue. The analyses of marls made by C. STRUCKMANN* were done in this manner.

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[*] The simplest way of ascertaining whether and what alkalies are present in a lime-stone, is the process given by ENGELBACH (Annal. d. Chem. u. Pharm. 123, 260)—namely, to ignite a portion of the triturated mineral strongly in a platinum crucible over the blast, boil with a little water, filter, neutralise with hydrochloric acid, precipitate with ammonia and carbonate of ammonia, filter, evaporate the filtrate to dryness, and examine the residue with the spectroscope. The carbonate of ammonia precipitate may be evaporated with hydrochloric acid to dryness, and examined in like manner for baryta and strontia.

[†] Pogg. Anal. 96, 145.

[‡] See Qual. Anal. § 146 6.

m. To effect the separation of the carbonate of lime, in hydraulic limes, from the silicates, DEVILLE† proposed to boil with solution of nitrate of ammonia, which he stated would dissolve the carbonate of lime, without exercising a decomposing action on the silicates. GUNNING‡ found, however, that by this process the double silicates of alumina and lime are more or less decomposed, with separation of silicic acid. As yet no method is known by which the object here stated can be accomplished with absolute accuracy.

Treatment of the sample with dilute acetic acid will sometimes give a good result, but generally *careful* treatment with dilute hydrochloric acid gives the best results. C. KNAUSZ § also recommends hydrochloric acid.

II. Volumetric Determination of Carbonate of Lime and Carbonate of Magnesia (for technical purposes).

a. If a mineral contains only carbonate of lime, the amount of the latter may be estimated from the quantity of acid required to effect its decomposition, the method described in § 223‖ being employed for the purpose. Or the carbonic acid in the mineral may be determined, say by the method described in Vol. I. p. 338, *bb*, and 1 eq. of carbonate of lime = 50 calculated for each eq. of carbonic acid = 22.

b. If, however, the mineral, besides carbonate of lime, contains carbonate of magnesia also, the results obtained by either process will give the amount of carbonate of lime + carbonate of magnesia, the latter being expressed by its equivalent quantity of carbonate of lime (that is, 50 of carbonate of lime for 42 of carbonate of magnesia). If, therefore, the actual amount of each has to be determined, it is necessary, in addition to the above determination, to estimate either the lime or the magnesia separately. For this purpose, one of the two following methods may be employed.

1. The dilute solution of 2 to 5 grams of the mineral is mixed with ammonia and oxalate of ammonia in excess, allowed to stand for 12 hours, and then filtered. The precipitate of oxalate of lime, together with the filter, is ignited, and the carbonate of lime produced is treated as directed in § 223. This process gives the amount of lime contained in the mineral analysed; the difference between this and the former result gives the amount of carbonate of lime equivalent to the amount of carbonate of magnesia present. In order to completely separate the lime from the magnesia two successive precipitations are indispensable (see § 154, 6, *a*).

2. 2 to 5 grams of the mineral is dissolved in the least possible excess of hydrochloric acid, and a solution of lime in sugar water added as long as a precipitate is formed. By this means the magnesia alone

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* Annal. d. Chem. u. Pharm. 74, 170.

† Compt. rend. 37, 1001; Journ. f. prakt. Chem. 62, 81.

‡ Journ. f. prakt. Chem. 62, 318.

§ Gewerbeblatt aus Würtemberg, 1855, Nr. 4; Chem. Centralbl. 1855, 244.

‖ This method, with some slight differences, was first proposed by BINEAU.

is precipitated. The precipitate is collected, washed, and treated as directed in § 223; the result represents the amount of magnesia present. The quantity of carbonate of lime equivalent thereto is deducted from the result of the total determination; the remainder is the amount of carbonate of lime present.

Method 2 is only suitable when the proportion of magnesia is small.

III. Analysis of Quick Lime and Cements.

Ordinary limestone, on suitable ignition, yields quick lime, which serves for the preparation of mortar and many other purposes; limestones which contain about 25 per cent. of clay, or—expressed in general terms—silicates capable of being decomposed by ignition with lime, yield cements by suitable heating. These are also obtained, as is well known, if, instead of limestones which contain clay in their natural condition, an artificially prepared mixture of clay with lime or carbonate of lime is heated.

The changes which occur on "burning" ordinary limestone, as well as that which contains clay, are the following:—

Water and carbonic acid are driven off, ferrous carbonate and carbonate of manganese become ferric oxide and oxide of manganese, organic matter is burnt, or at least is decomposed, leaving a small residue of carbon; but, above all, the intermixed silicates are split up, so that their bases become soluble in hydrochloric acid, whilst their silica, on treatment with hydrochloric acid, is partly dissolved and partly separates as hydrate. Intermingled quartz, on the other hand, undergoes scarcely any change on heating. If quick lime or cement is exposed to the action of the air, it gradually absorbs water and carbonic acid.

Of course no mention is made in this work of technical tests, whereby the suitability of limes and cements for building purposes is ascertained,* but the following remarks may be made with reference to the most suitable methods for their analysis:—

1. A few grams may be ignited in a platinum crucible over the blowpipe. The loss of weight gives the *water* and *carbonic acid.*

2. In a larger sample (about 10 grams), the *carbonic acid* may be determined by the method given in Vol. I. p. 340. The amount of *water* is found by the difference, or it may be determined directly (§ 235, I. *e*).

3. About 5 grams are treated with dilute hydrochloric acid in excess, and evaporated down to dryness in a platinum or porcelain dish; the residue is then moistened with hydrochloric acid, warmed, water is added, and the undissolved portion is collected and washed (§ 140, II. *a*).

4. The contents of the filter in 3 are washed into a dish, without damaging the filter, boiled with successive quantities of a concentrated solution of carbonate of soda, and filtered through the same filter fitted in a hot-water funnel, until all the hydrated silica is dissolved (that is, until a few drops remain clear after being heated with solution of chloride of ammonium), and the residue is washed. The *silica* is separated from the alkaline solution by § 140, II. *a*, *ab*. The

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* W. MICHAELIS' gives excellent advice on this point in his work, "Zur Beurtheilung des Cementes," Berlin, polytechnische Buchhandlung, A. Seidel, 1876.

residue, which is insoluble in the carbonate of soda, consists of *quartz-sand* and a residue of *undecomposed silicate.* This is washed into a platinum dish, the ash of the filter-paper is added, and the water evaporated down to a small bulk, and allowed to cool; sulphuric acid is then added, and the mixture heated for some time. By this means the bases are dissolved, and the silica, which has been separated from them, may now be washed out from the sand by treating the undissolved washed residue with a solution of carbonate of soda. In the sulphuric acid solution, the portions of alumina, ferric oxide, &c., present are determined. If treatment with sulphuric acid in open vessels should not be successful, the heating with sulphuric acid is done in sealed tubes (Vol. I. p. 354).

5. The hydrochloric acid solution obtained in 3 is made up to 500 c.c., and the *sulphuric acid*,* *potash*, and *soda* (§ 209, 4) are determined in 250 c.c. The *ferric oxide* (*oxide of manganese*) and *alumina* are estimated in the other 250 c.c. by repeated precipitation with ammonia (§ 235, I. *c*). The filtrate is made up to 500 c.c., and the *lime* and *magnesia* are determined in 250 c.c. of it (§ 154, 6).

8. ALUMINIUM COMPOUNDS.

A. Clays.

(See Silicon Compounds, § 238.)

B. Sulphate of Alumina.

§ 236.

Of the compounds of alumina, sulphate of alumina will be first considered. It is manufactured on a large scale by various methods (latterly more especially by treating with sulphuric acid, the hydrate of alumina obtained from cryolite or bauxite), and comes into the market, generally in the state of solid crystalline cakes, containing various amounts of water; it is of different degrees of purity, and is therefore often the subject of chemical analysis.

1. The quantity of water, which may amount to 40 or 50 per cent., cannot be determined accurately by direct heating, because the water that is driven off has an acid reaction. If, therefore, this is to be determined by loss of weight, the sulphate of alumina (about 0·5 gram) must be ignited with pure oxide of lead (§ 35, β). The water may be determined directly by ignition of the sulphate of alumina with anhydrous carbonate of soda (§ 225, I.). It should be noted that both these methods of determining the water, give, besides the water of crystallisation, also the water in any acid alkaline sulphate, or hydrated sulphuric acid which may be present.

2. About 12 grams is dissolved in water. If an *insoluble residue* remains, it should be filtered off, ignited, and weighed. The solution is made up to 500 c.c.

3. 150 c.c. of the solution is diluted, a little hydrochloric acid added, and precipitated hot with chloride of barium (§ 132, 1) in slight excess

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* Cements generally contain this, see W. MICHAELIS' "Die hydraulischen Mörtel, insbesondere der Portland Cement," p. 89, Leipzig, Quandt. u. Händel, 1869.

only. The total amount of *sulphuric acid* is determined from the sulphate of baryta obtained.

4. The alumina and the excess of baryta are then precipitated from the filtrate obtained in 3 by ammonia and carbonate of ammonia, the pure chlorides of the alkaline metals (§ 225, II. *e*) are extracted from the filtrate, and, lastly, the amount of *potash* contained in these is determined. As a rule, the preparations at present coming into the market only contain soda.

5. Chloride of ammonium is added to 100 c.c. of the solution obtained in 2, the solution precipitated with ammonia (§ 105, *a*), the precipitate after moderate washing dissolved in hot hydrochloric acid and the diluted solution again precipitated with ammonia. The weight of the thoroughly washed and ignited precipitate represents the amount of *alumina* together with the *ferric oxide* which is sometimes present.

6. 200 c.c. of the solution obtained in 3 is gradually added to a hot, tolerably concentrated solution of potash or soda, and then more of the alkaline solution is added, until the precipitated hydrate of alumina is redissolved. After prolonged heating there still remains, as a rule, a slight undissolved precipitate. The solution is diluted, filtered, washed through, and the precipitate dissolved in hot hydrochloric acid; the solution is then heated, precipitated with ammonia, heated until the liquid has only a feeble alkaline reaction, filtered and the small quantities of *lime* and *magnesia* determined in the filtrate, if they are present. In the precipitate, which generally contains a little alumina, the *ferric oxide* is determined by § 160, A, 2.

7. All the bases are calculated as neutral sulphates ($Al_2O_3,3SO_3$; $Fe_2O_3,3SO_3$; NaO,SO_3, &c.) and the amount of sulphuric acid contained in them is subtracted from that obtained in 3; there is then generally a small remainder, which, as far as the quantity of alkaline sulphates is concerned, is to be considered as combined with a corresponding amount of these to form acid alkaline sulphates; in the other case, the excess of sulphuric acid would be expressed as hydrated sulphuric acid. If the sulphuric acid which will neutralise alkali (such as that combined with alumina and lastly with ferric oxide, as well as that which is combined with neutral alkaline sulphate to form acid sulphate or is present in the free state) is to be determined as an acidimetric control, it must be performed according to this vol. p. 201, *c*.

9. SILICON COMPOUNDS.

A. Analysis of Native and, more particularly, of mixed Silicates.*

§ 237.

The analysis of silicates which are completely decomposed by acids has been described in § 140, II. *a*; and that of silicates which are not decomposed by acids, in § 140, II. *b*. It is only necessary, therefore, to add here a few remarks respecting the examination of mixed silicates, that is, of such as are composed of silicates of the two classes (phonolites, clay-slates, basalts, &c.).

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* Comp. Qual. Anal. §§ 205–208. The quantitative analysis must always be preceded by a minute and comprehensive qualitative analysis.

1. A homogeneous, air-dried, finely powdered sample is prepared, and the *moisture* in it determined by drying 1 to 2 grams at 120° until the weight is constant.

2. Another sample of the air-dried substance is usually treated for some time, at a gentle heat, with moderately concentrated hydrochloric acid, evaporated to dryness on the water-bath, the residue moistened with hydrochloric acid, water added, and the solution filtered; it is often preferable, however, to digest the powder with dilute hydrochloric acid (of about 15 per cent.), for some days at a gentle heat, and then at once filter the solution. Which of the two ways it may be advisable to adopt, or indeed whether the method here described (which was first employed by C. GMELIN in the analysis of phonolites) can be resorted to, depends on the nature of the mixed minerals. The more readily decomposable the one of the constituent parts of the mixture is, and the less readily decomposable the other, the more constant is the proportion between the undissolved and the dissolved portions in different experiments; in other words, the less the undissolved part is affected by further treatment with hydrochloric acid, the more safely may this method of decomposition be resorted to.

The process gives :—

a. A *hydrochloric acid solution*, containing, besides more or less silicic acid, according to circumstances, the bases of the decomposed silicate in the form of metallic chlorides; these, after the removal of the silicic acid (§ 140, II. *a*), are separated and determined by the methods given in the fifth section.

b. An *insoluble residue*, which contains, besides the undecomposed silicate, the separated silicic acid of the decomposed silicate.

After the latter has been well washed with water to which a few drops of hydrochloric acid have been added, it is transferred, while still moist, in small portions at a time, to a boiling solution of carbonate of soda free from silicic acid, contained in a platinum dish; it is boiled for some time, and filtered each time, while still very hot (a hot-water funnel is most convenient), through a weighed filter. Finally, the last particles of the residue which still adhere to the filter are rinsed into the dish. If this operation cannot be successfully carried out, the filter is dried and incinerated, the ash transferred to the platinum dish, and boiled repeatedly with the solution of carbonate of soda, until a few drops of the liquid finally passing through the filter remain clear on warming with excess of chloride of ammonium. The insoluble residue is washed first with hot water, then—to insure the removal of every trace of carbonate of soda which may still adhere to it—with water slightly acidified with hydrochloric acid, and finally again with pure water.

The alkaline filtrate is acidified with hydrochloric acid, and the silicic acid which belongs to the silicate decomposed by hydrochloric acid, is determined in it as directed in § 140, II. *a*. The undissolved silicate is dried at 120°, and weighed. If the weight of this, together with that of the moisture, be subtracted from the weight of substance originally taken, the difference will give the quantity of the dissolved silicate in a dry state. The undissolved silicate is treated exactly as directed in § 140, II. *b*.

3. Silicates dried at 120° occasionally contain *water*. This is determined by taking a weighed portion of the mixed silicate dried at 120°

(see 1) and igniting it in a platinum crucible, or, in presence of carbon or protoxide of iron, in a tube, through which a stream of dry air is drawn, the moisture expelled from the substance being retained by a weighed chloride of calcium tube. To ascertain whether the water thus expelled proceeds from the silicate decomposable by hydrochloric acid, or from that which hydrochloric acid fails to decompose, a sample of the latter, dried at 120°, is also ignited in the same manner. Suppose, for instance, the mixed silicate under examination consists of 50 per cent. of silicate decomposed by hydrochloric acid, and 50 per cent. of silicate which hydrochloric acid fails to decompose; and that the latter contains 47 parts of anhydrous substance, and 3 parts of water; the determination of the water would give, for the mixed silicate 3 per cent., for the portion not decomposed by hydrochloric acid 6 per cent. Now, as 3 bears the same proportion to 6 as the undecomposed silicate (50 per cent.) bears to the mixed silicate (100 per cent.), it is clear that the silicate decomposed by hydrochloric acid gives no water on ignition.

If the escaping aqueous vapours have an acid reaction, owing to disengagement of *hydrochloric acid* or *fluoride of silicon*, the finely powdered substance is mixed with dry carbonate of soda and ignited in a current of dry air, and the water evolved is received in a weighed chloride of calcium tube (§ 36). The best method of conducting this determination of water in silicates has been thoroughly studied by E. LUDWIG* and L. SIPÖCZ.† The former ignites the mixture in an expanded platinum tube, the latter in a platinum boat. SIPÖCZ recommends the following method of procedure:—Heat strongly 4 parts of carbonate of potash and soda in a platinum dish, allow it to cool to 50—60°, mix intimately, by means of a platinum wire, the weighed, powdered, and dried silicate (1 part), place the mixture in a capacious platinum boat and rinse out the dish with a little carbonate of potash and soda. The boat, loosely covered with a lid with overlapping edges, is now pushed into the middle of a porcelain tube, glazed inside, 400 mm. long and of 17 mm. internal diameter, and this is heated at 120—130° for an hour in an air-bath. The tube is connected at one end with a gas-holder with intermediate soda-lime and sulphuric acid tubes, and at the other end with a chloride of calcium tube, a tolerably rapid current of air being passed through the whole apparatus. When by this means every trace of moisture is removed, the tube is placed in a combustion furnace, so that it is heated directly by the flames, and a weighed U-tube containing glass beads, moistened with pure sulphuric acid, is substituted for the chloride of calcium tube. The current of air must be properly regulated, and the tube heated gradually to low redness, at which it is maintained for about half an hour.

According to SAINTE-CLAIRE DEVILLE and FOUQUÉ,‡ by properly conducting the ignition of silicates containing fluorine compounds, the water may usually be expelled free from the latter, since they require a far higher temperature for expulsion than the water does. After the water has been driven off, the fluorine is expelled if the

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[*] "Untersuchung über die chemische Zusammensetzung des Pyrosmaliths" mineralog. Mittheilungen von G. TSCHERMAK, 1875, 211 (Zeitschr. f. anal. Chem. 17, 206).

[†] Zeitschr. f. anal. Chem. 17, 207.

[‡] Compt. rend. 38, 317; Journ. f. prakt. Chem. 62, 78.

substance is strongly ignited, either as alkaline metallic fluoride or as fluoride of silicon.

4. The undecomposed part of a mixed silicate occasionally contains *carbonaceous organic matter*, in which case it is the safest way to treat an aliquot part of it in a current of oxygen gas, and weigh the carbonic acid produced (§ 178). According to DELESSE, traces of nitrogen are almost invariably present in the organic matter contained in silicates.

5. Silicates often contain admixtures of other minerals (magnetite, pyrites, apatite, carbonate of lime, &c.), which may sometimes be detected by the naked eye or with the aid of a magnifying glass. It would be a somewhat difficult undertaking to devise a method generally applicable to all cases of this description; but it may be noted that it is occasionally found to be advantageous first to treat the substance with acetic acid, before submitting it to the action of hydrochloric acid; in this way, in particular, the separation of the carbonates of the alkaline earths may be effected without the least difficulty. Some analyses by DOLFUSS and NEUBAUER,* which were made in the author's laboratory, may be cited as examples of complete examinations of this kind.

6. If *sulphides* are present in the silicate, the sulphur is determined by one of the methods given in § 148, II. *A*, by the dry way, or, which is preferable as a rule, in the wet way; or CARIUS' method may be employed (this vol. p. 65). As regards the methods in the wet way, it must be borne in mind that, if baryta, strontia, or lead be present, a portion of the sulphuric acid produced will remain in the insoluble residue; this, however, is not the case when the mineral is fused with alkaline carbonate and nitrate. If a *sulphate* is present along with sulphides, the sulphuric acid in the former is determined by boiling a separate portion of the substance with a solution of carbonate of potash or soda for a long time, filtering, acidifying the filtrate, and precipitating with chloride of barium. The sulphuric acid thus found is deducted from that obtained after treatment with oxidising agents, and the difference gives the sulphur in the sulphide. In many cases, extracting the substance with hydrochloric acid is preferable to boiling with carbonate of soda for the determination of sulphuric acid in sulphates.

7. The *iron*, which is almost always found in silicates, may be present in the ferrous or ferric state, or in both. As the solution of this question is of great importance in the discrimination of a mineral, and the accurate determination of the ferrous oxide in silicates is beset with many difficulties, it is a subject which has been frequently investigated and much worked at. The following are of importance:—

a. HERRMANN'S method. Decomposition of the mineral by fusion with borax in a current of carbonic acid; this gives an amount of ferrous oxide which is too high, and is to be rejected (RAMMELSBERG,† SUIDA ‡).

b. In many cases the object is attained by heating some of it in sealed glass tubes with hydrochloric or sulphuric acid (Vol. I. p. 354, *e*), and determining the ferrous oxide in the solution by chromate or permanganate of potassa, or the ferric oxide volumetrically by stannous chloride.

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* Journ. f. prakt. Chem. 65, 199.

† Zeitschr. der deutsch. geologischen Gesellsch. 1872, 69.

‡ Zeitschr. f. anal. Chem. 17, 212.

c. In those cases where *b* does not give the results desired, or generally in all cases, a solution suitable for the titration of the ferrous or ferric oxide may be obtained by decomposing the substance with hydrofluoric acid and sulphuric acid, or with hydrofluoric acid and hydrochloric acid. The treatment often answers well in open vessels, with exclusion of air; see Vol. I. p. 213.* If the hydrofluoric acid contains reducing substances (arsenious acid [C. JEHN†]), sulphuretted hydrogen, sulphurous acid, &c.), it must be decomposed with permanganate of potassa, and distilled from a platinum retort (E. LUDWIG). In order to avoid this operation, DÖLTER (*loc. cit.*) recommends evaporating the solution obtained by decomposing the substance with hydrofluoric acid and sulphuric acid, in an atmosphere of carbonic acid, in order to drive off the excess of hydrofluoric acid, and with it the reducing sulphur compounds contained in it, and then to titrate. In this case, however, those errors are not excluded, which arise from the reducing substances present in the hydrofluoric acid which directly reduce ferric oxide during the dissolution.

In the case of silicates which are only decomposed with great difficulty, the very finely powdered substance is treated with *pure* hydrofluoric acid and moderately dilute sulphuric acid in sealed tubes of Bohemian potash glass. In order to obtain very accurate results, SUIDA‡ recommends treating in exactly the same manner similar quantities of the same hydrofluoric acid and sulphuric acid in a piece of the same glass tube by the side of that containing the substance to be decomposed, and subtracting the quantity of permanganate of potassa required to colour this liquid from the quantity used for the decomposed substance.

8. If silicates contain small quantities of *titanic acid*, as is very frequently the case, care must be taken not to overlook this admixture. If the silicic acid has been separated by evaporation with hydrochloric acid, and that whether the silicate has been decomposed by hydrochloric acid or has been previously submitted to the action of carbonated alkali, the titanic acid, or at least by far the greater part of it, will be found, as a rule, in the hydrochloric acid solution.

In order to test the separated silica for titanic acid, it is treated with hydrofluoric acid and a little sulphuric acid in a platinum dish, evaporated, the residue fused with bisulphate of potash, the melt dissolved in cold water, the solution filtered if necessary, and the titanic acid separated from the sulphuric acid solution by the method given in § 107, 2.

The chief portion of the titanic acid is usually contained in the hydrochloric acid solution filtered from the silicic acid, and is thrown down with the ferric oxide and alumina, when ammonia is added (§ 161, 4). In this precipitate, it may be determined either by igniting the precipitate in a current of hydrogen, extracting the reduced iron by digestion with dilute nitric acid (Vol. I. p. 441, 7, *a*), fusing the residue with bisulphate of potash, taking up with cold water, and precipitating the titanic acid by boiling (§ 107); or by at once fusing the precipitate of ferric oxide, alumina, and titanic acid with bisulphate of potash, dissolving in cold water, neutralising the solution as nearly as possible with carbonate of soda, and diluting with water, so that not more than 0·1 gram of the oxides is contained in 50 c.c. Hyposulphite of soda in slight excess is now added to the cold solution, waiting until the liquid, which was at first violet, has become quite colourless, and consequently the whole of the ferric oxide is reduced to the ferrous state, boiling until sulphurous acid ceases to be disengaged, filtering, washing the precipitate with boiling water, drying, gently igniting in a covered porcelain crucible, to expel sulphur, then taking off the lid and increasing the heat. In this way the alumina (CHANCEL*) and the titanic acid (A. STROMEYER†) are obtained free from ferric oxide, and may be separated by the method given above. In the separation of titanic acid by boiling the sulphuric acid solution, the operation must be conducted very cautiously (see § 107), or the titanic acid will not be completely precipitated; see RILEY.‡ In order to precipitate perfectly pure titanic acid by boiling, from solutions containing iron, G. STREIT and B. FRANZ § recommend the addition of about an equal volume of acetic acid.

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* With reference to other apparatus for this purpose see COOKE, Zeitschr. f. anal. Chem. 7, 98; WILBUR and WHITTLESEY, *Ibid.* 10, 98; A. R. LEEDS, *Ibid.* 16, 323; DÖLTER, *Ibid.* 18, 53.

† Zeitschr. f. anal. Chem. 13, 176.

‡ *Ibid.* 17, 213.

9. If the silicates contain boric acid, a method proposed by A. DITTE || may be employed for its determination instead of that given in Vol. I. p. 500, 5, *b*; this method is based on the separation of the boric acid in the form of borate of lime, which is allowed to crystallise from a fused mixture of chloride of calcium, chloride of sodium, and chloride of potassium. See Appendix.

10. The determination of the chlorine, fluorine and phosphoric acid in silicates has already been sufficiently described in §§ 166 and 167.

11. Amongst the most complicated analyses of silicates is that of meteorites, in which uncombined metals, metallic sulphides, phosphides, and carbides, as well as chrome iron ore, are present along with silicates. With regard to their examination, which occurs but seldom, the treatise on the analysis of the Zsadányer meteorites by W. PILLITZ ¶ may be consulted, where the most advantageous method of examination is accurately described.

12. The analysis of ultramarine also presents unusual difficulties. For the most suitable methods, REINHOLD HOFFMANN's comprehensive work on ultramarine may be consulted.**

13. If a silicate which is not decomposed by acids contains an admixture of quartz, and if the amount of this ingredient is to be determined separately, one of the methods described in § 238, II. *f*, may be adopted.

The analysis of clay, about to be described, may be performed by a mode of procedure differing slightly from the methods of silicate analysis just detailed.

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* Compt. rend. 46, 987; Annal. d. Chem. u. Pharm. 108, 237.

† Annal. d. Chem. u. Pharm. 113, 127.

‡ Journ. Chem. Soc. 15, 311; Zeitschr. f. anal. Chem. 2, 70.

§ Journ. f. prakt. Chem. 108, 65; Zeitschr. f. anal. Chem. 9, 388.

|| Ann. Chim. Phys. [5] 4, 549; Zeitschr. f. anal. Chem. 14, 360.

¶ Zeitschr. f. anal. Chem. 18, 58.

** "Ueber Ultramarin," 1873, Frankfort, R. Baist; WAGNER's Jahresber., 1873, 378 *et seq.*

B. Analysis of Clays.

§ 238.

The several varieties of clay, derived from the disintegration, that is, the mechanical separation and chemical decomposition of rocks containing silicate of alumina, such as felspar and clay shale, consist commonly of a mixture of true clay with quartz- or felspar-sand, and often contain the liberated silicic acid, which may be extracted by means of boiling solution of carbonate of soda. If the clays are no longer in the locality where they were found, they are usually less pure, and contain admixtures of various minerals, and, as a rule, organic matter also.

With regard to the various technical uses of the material in question, it is a matter of importance to know not only its chemical composition, but also the constituents into which it can be separated by mechanical means. It is better, therefore, to make a mechanical analysis before proceeding to the chemical analysis.*

I. Mechanical Analysis.

By the aid of mechanical analysis we are enabled to determine the quantities of coarse sand, fine sand, and of the finest portions which can be removed by elutriation (clay), which form the constituent parts of the natural clays.

The mechanical analysis of clays has lately been repeatedly worked at. The washing apparatus, with which it is performed, is improved, and the constituent parts of the clay which can be mechanically separated are more sharply defined. SCHÖNE'S† is recognized as the best washing apparatus; this has been slightly modified by W. SCHÜTZE‡ for washing clay, and the component parts of the clay which can be mechanically separated, have been more accurately defined by SEGER;§ thus—coarse sand: all with the size of grains over 0·20 mm.,—medium sand: size of grains 0·04 to 0·20 mm.,—dust sand: size of grains 0·02 to 0·44,—marly clay: size of grains 0·01 to 0·20 mm.,—clay: all the finer portion.

In spite of all these improvements, the mechanical analysis of clay is always somewhat incomplete. Thus, the dust sand obtained by SEGER,|| by means of SCHÖNE'S washing apparatus, from the clay of Senftenburg contains 9·3 per cent. of alumina, and that similarly obtained from the Ardennes clay as much as 25·32 per cent.

On this account those who are engaged in working specially on the mechanical analysis of clay, are referred to the treatises quoted; but particularly to CARL BISCHOF'S comprehensive and admirable work, "Die feurfesten Thone,"¶ &c., in which pages 74 to 86 treat of the analysis of clay by elutriation.

For most purposes, separation of the clay by the simple method of washing, as employed by the author in the investigation of the Nassau clay quoted above, and which will be described below, is sufficient.

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* Compare the author's "Untersuchung der wichtigsten nassauischen Thone," Journ. f. prakt. Chem. 57, 65.

† Zeitschr. f. anal. Chem. 7, 20.

‡ Notizblatt für Fabrikation von Ziegeln, &c. 1872, 188.

|| *Ibid.* 1873, 109.

§ Zeitschr. f. anal. Chem. 9, 397.

¶ Leipzig, Quandt u. Händel, 1876.

For this purpose, the elutriating apparatus is employed which F. SCHULZE* has recommended for the mechanical analysis of soils, and which, if not perfect, is very convenient and particularly simple. The more perfect, but at the same time more complicated, washing apparatus of SCHÖNE, already referred to, in the analysis of soils, may also be employed.

For the analysis of soils by elutriation F. SCHULZE employs—

a. A glass of the form of a champagne glass, 200 mm. deep, and 70 mm. in diameter at the mouth, on which a brass ring is cemented, 15 mm. broad, with a tube slightly inclined downward, proceeding from its side.

b. A funnel tube; the diameter of the funnel should be 50 mm., the tube should be 400 mm. long, and about 7 mm. in diameter. It is drawn out at the point so that the mouth may be only 1·5 mm. in diameter.

c. A vessel of, at least, 10 litres capacity, filled with water. The best material for this vessel is sheet zinc; it should have an aperture at the top for pouring in the water, and a lateral opening at the bottom with stop-cock. It is placed upon a support, movable up and down. The funnel tube is suspended from the cock by means of a small cord, so that the mouth may be in or directly above the funnel.

d. A dish, or large beaker, to receive the liquid running from the discharge tube.

Thirty grams of the air-dried clay under examination is crushed, transferred to a porcelain dish, 2 to 3 times its bulk of water added, and the mixture boiled for an hour, with gentle rubbing with a pestle, in order to effect complete separation of the component parts of the clay. The boiled mass is allowed to cool, and, when cold, the contents of the dish is washed into the elutriating glass, *a*, the cock of the vessel *c* is opened a little, and the funnel tube *b* inserted, with the jet of water issuing from it, into *a*, taking care to have the point of the tube a few millimetres above the deepest part of the glass, which may be effected either by lowering the support of the vessel *c*, or by placing the elutriating glass higher. The cock is regulated so that the water always fills the funnel about half full; under these circumstances the pressure of the water, that is, the difference of level in the elutriating glass and the funnel tube, is about 200 mm.

By the force of the jet of water, the particles of clay are violently stirred up; but only the finer of them are thrown up sufficiently high to reach the lateral opening at the top of the glass, and thus to be carried off through the discharge tube and conveyed into the dish or beaker, *d*; the coarse sand remains in the elutriating glass. When the water runs off almost clear from the discharge tube, the cock is shut, the elutriating glass removed, and the still somewhat turbid liquid rapidly decanted from the coarse sand into the dish; the deposited sand is then rinsed with the aid of a washing bottle with jet directed upward, into a small dish, dried, ignited, and weighed.

The turbid liquid in the dish or beaker is allowed to settle for at least 6 hours, the clear or still turbid supernatant portion is then decanted, and the deposit, which is now sure to contain the whole of the fine sand, is washed into the elutriating glass, where the process of elutriation is repeated, taking care, however, to restrict the flow of water from the vessel *c* to a mere dropping on to the side of the funnel, so that the column of water in the funnel tube stands only about 30 mm. higher than in the elutriating glass; this operation is continued until the water passing off through the discharge tube is quite clear, which generally takes 3 to 4 hours. The residual fine sand is then treated in the same way as the coarse sand above.

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* Journ. prakt. Chem. 47, 241.

The water is now determined in another weighed portion of the air-dried clay, by long ignition, and the amount of the very finest particles separable by elutriation (the clay proper) is calculated from the difference.

The following analyses of the author's, made on the poor clay of Hillscheid and the far fatter clay of Ebernhahn, may be quoted as examples of the results yielded by this method :—

	Hillscheid Clay.	Ebernhahn Clay.
Coarse sand . . .	24·68	6·66
Fine sand	11·29	9·66
Clay	57·82	74·82
Water	6·21	8·86
	100·00	100·00

II. Chemical Analysis.

The quantitative analysis should be preceded by a *qualitative examination* which must be sufficiently extended to show what substances pass into the aqueous solution on boiling the clay with water and allowing it to stand for some time to clear (chloride of sodium, chloride of ammonium, sulphate of lime, ferrous sulphate, organic substances, &c.), and what are dissolved on treatment with very dilute hydrochloric acid at a gentle heat (carbonate of lime, carbonate of magnesia, ferric oxide, phosphoric acid, &c.). According to circumstances, the clay is submitted to quantitative analysis either as it is, or after it has been freed from intermixed carbonates of the alkaline earths by treatment with weak acids (acetic acid, very dilute hydrochloric acid), or after the coarser sand has been separated from it by washing.

First Method.

a. The air-dried clay is powdered as finely as possible and placed in a stoppered sample tube.

b. About 2 grams of the sample is dried in a platinum crucible or platinum dish at 120° until the weight is constant; the loss in weight gives the moisture. The clay is then ignited, at first gently, and afterwards strongly and for a tolerably long time; the loss in weight corresponds with the combined water (together with the organic and volatile constituents of the clay, if such are present).

c. 1 to 2 grams of the air-dried clay is decomposed with carbonates of soda and potassa and treated exactly according to § 140, II. *b.* The *silicic acid* obtained is, after weighing, volatilised by treatment with fluoride of ammonium and sulphuric acid. If there is a residue which cannot be volatilised in this way, it must be subtracted from the weight of the impure silica. The residue is fused with acid sulphate of potassa, and in the solution the *titanic acid* (§ 237, 8), which is sometimes present, and the alumina which is occasionally present in small quantity, are determined.

d. After filtering off the silicic acid from the hydrochloric acid solution, the latter is evaporated, with the addition of a few drops of nitric acid, until the greater portion of the free acid is expelled; it is then diluted with water, mixed with pure carbonate of baryta in excess, and the mixture allowed to digest for 24 hours in the cold, with repeated stirring; the precipitate, which consists of hydrate of alumina, a little hydrated ferric oxide, and carbonate of baryta, is collected and washed first by decantation, then on the filter. The washed precipitate is dissolved in hydrochloric acid, the baryta precipitated by sulphuric acid, the precipitate collected, washed, the washings added to the filtrate, and the latter divided into two equal portions, *a* and *β*.

- *a*. Is precipitated with ammonia, allowed to stand for some time in a warm place, and then filtered; the precipitate is thoroughly washed, dried, and ignited finally by means of the blast gas-lamp. The ignited precipitate is weighed, and the weight multiplied by 2; the result is alumina + ferric oxide.*
- *β*. Is concentrated and the ferric oxide determined with stannous chloride (Vol. I. p. 225), or mixed with tartaric acid, ammonia, and sulphide of ammonium, and the iron estimated as oxide (Vol. I p. 435, **77**). The ferric oxide obtained must be multiplied by 2.

The alumina = the result of *a*, *minus* the result of *β*, and (in the event of such being found) *minus* the small quantities of titanic and silicic acids which were obtained in *a*, and which of course are to be first multiplied by 2.

The filtrate from the precipitate produced by carbonate of baryta is cautiously mixed, without previous concentration, with sulphuric acid (§ 132, 1), the sulphate of baryta collected, and washed until the washings are quite free from sulphuric acid, the filtrate is then concentrated, but not sufficiently to cause separation of sulphate of lime; the lime and magnesia are separated as directed in § 154, 6 (**36**).

e. 1 to 2 grams of the clay dried at 100°, after addition of sulphuric acid, is treated either with strong aqueous hydrofluoric acid (Vol. I. p. 350) or with gaseous hydrofluoric acid (Vol. I. p. 351), or with fluoride of ammonium (Vol. I. p. 352). The sulphates, in whichever way they have been obtained, are treated with hydrochloric acid. If anything remains undissolved, it is allowed to settle, the clear liquid poured off as far as possible, and the residue again treated with hydrofluoric acid or fluoride of ammonium. To the dilute hydrochloric acid solution, chloride of barium is cautiously added as long as a precipitate forms, and then, without filtering, carbonate of ammonia and some ammonia. The precipitate is allowed to settle in the cold, collected, and washed, the filtrate evaporated to dryness, and the residue ignited to expel the ammonia salts; after being taken up with water, the solution is boiled with some milk of lime to remove the magnesia, filtered, and the lime and any baryta that may remain in solution removed by ammonia, carbonate of ammonia, &c. The alkalies are then determined as directed (this vol. p. 155).

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* This precipitate usually contains the greater portion of the titanic acid that may be present, if the method described in the preceding paragraph (p. 263) has been employed. Should an insoluble residue remain on fusion with bisulphate of potash and treatment with water, this consists of silicic acid. This should be flocculent in appearance, otherwise this residue must be again fused with bisulphate of potash or treated with carbonate of soda (§ 140, II. *b*).

The foregoing processes give the gross composition of the clay, but in order to ascertain how much of the silicic acid found exists in combination with the bases of the clay, A; how much as hydrated acid, B; and how much as quartz sand, or as a silicate present in the form of sand (felspar sand, for instance), C; the following processes are required.

f. A third portion, 1 to 2 grams, of the air-dried clay is heated for 10 to 12 hours with an excess of pure sulphuric acid, to which a little water has been added, finally expelling nearly the whole of the excess of acid. It is then allowed to cool, water added, the undissolved residue (A + B + sand) washed, transferred while still moist to a platinum or porcelain dish, and treated with boiling solution of carbonate of soda, as directed in § 237, 2, *b.* By estimating the silicic acid dissolved in the alkaline solution, A + B is ascertained. The undissolved sand is collected, washed, ignited, and weighed. If the weight of the sand, together with A + B, is equal to the total amount of silicic acid found in *c*, the sand is pure quartz sand; but if it is greater, the sand is not pure quartz sand, but consists of the more or less sandy powder of a silicate, such as felspar sand; in the latter case, C is found by subtracting A + B from the total quantity of the silicic acid found in *c.* If the nature of the sandy silicate has to be ascertained, a special analysis of the separated sand must be made.

The quartz sand may be separated from the silicates which are mixed with it, by heating it in a sealed glass tube with slightly diluted sulphuric acid (Vol. I. p. 354), or by cautiously heating with phosphoric acid, which as the temperature is gradually increased first decomposes the silicates with separation of gelatinous silica, and then attacks the quartz (A. Müller *). The heating must be very cautiously regulated, and be stopped at 190° to 200°. A. Müller has devised a suitable oven for this purpose;† E. Laufer's communication ‡ shows this and also to what extent quartz sand is attacked by heating with phosphoric acid.

g. To ascertain the amount of silicic acid which a boiling solution of carbonate of soda will remove from the clay, B, and which may be assumed to be present as hydrated silicic acid, a somewhat larger weighed portion of the sample is dried, repeatedly boiled with the solution in question, and the silicic acid in the filtrate is determined by evaporation with hydrochloric acid. Finally, A = (A + B) − B.

h. If clays contain appreciable quantities of organic substances or metallic sulphides, these are determined by § 237, 4, but the amount of sulphur contained in them is estimated by § 237, 6.

Second Method.

The analysis of clays composed of quartz sand, and of clay readily decomposed by sulphuric acid, may be effected by the following much less complicated method :—

a. Preparation for analysis, drying, and estimation of water, the same as in the first method.

b. About 2 grams of the clay is decomposed with sulphuric acid, as in *f* of the first method; the greater part of the sulphuric acid is removed by evaporation, the mixture diluted with water, the silicic acid and sand filtered off, and the silicic acid separated from the sand by means of a solution of carbonate of soda, both being determined as in § 237, 1, *b*.

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* Zeitschr. f. anal. Chem. 5, 431.

† *Ibid.* 7, 465.

‡ *Ibid.* 17, 368.

c. To the filtrate from *b*, a solution of nitrate of lead is cautiously added, taking care to avoid any considerable excess; after several hours the sulphate of lead is collected, washed, the washings added to the filtrate, and the last trace of lead removed from the latter by sulphuretted hydrogen; the solution is filtered, the filtrate evaporated, finally in a small dish, and the residue treated as directed in § 161, 5 (**118**). As clay rarely contains weighable traces of manganese, this method is reduced to a few simple operations.

10. CHROMIUM COMPOUNDS.

Analysis of Chrome Iron Ore.

§ 239.

This mineral is essentially a compound of ferrous oxide with sesquioxide of chromium; occasionally a portion of the latter is found replaced by ferric oxide and alumina, and of the former by magnesia. In addition to these compounds, silicates and small quantities of lime, manganese, titanic acid, &c., are met with. As the amount of chromium it contains varies greatly, it is often necessary, in order to ascertain its value, to subject it to chemical analysis. Since chrome iron ore is not so easily decomposed as most other minerals, many chemists have made investigations to find out the most suitable methods for this purpose. As a knowledge of these is instructive, a list of the most important papers on the subject that have appeared lately is given in the foot-note,* only the best and simplest methods being described in detail. These include both estimation of the chromium and also the accurate determination of all the substances present.

As a preliminary, it is necessary in all the methods to reduce the ore to an impalpable powder. This operation must be performed with patience and conscientiously, for on it depends the success of the analysis.

CHRISTOMANOS recommends igniting the coarse powder in a platinum dish for a short time, but strongly, in order to facilitate the powdering in the agate mortar. Finally the powder must be separated from all rather coarser portions by sifting, and these must be again powdered and mixed in. Elutriation is inadmissible, as it renders the sample uneven. If the method of powdering recommended by CHRISTOMANOS is employed, the sifted powder is again heated before weighing. The analysis is then performed on the anhydrous substance.

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* P. HART (Journ. prakt. Chem. 67, 320), CALVERT (Dingl. polyt. Journ. 125, 466), C. O'NEILL (Chem. News, 1862, No. 123, 199; Zeitschr. f. anal. Chem. 1, 497), OUDESLUYS (Chem. News, 1862, No. 127, 254; Zeitschr. f. anal. Chem. 1, 498), T. S. HUNT (Sill. Am. Journ. [2] 5, 418), F. A. GENTH (Chem. News, 1862, No. 137, 32; Zeitschr. f. anal. Chem. 1, 498), GIBBS and P. C. DUBOIS (Zeitschr. f. anal. Chem. 3, 401), F. W. CLARKE (Zeitschr. f. anal. Chem. 7, 463), J. BLODGET BRITTON (Chem. News, vol. 21, 266; Zeitschr. f. anal. Chem. 9, 487), F. C. PHILLIPS (Zeitschr. f. anal. Chem. 12, 189), F. H. STORER (*ibid*. 9, 71; similarly F. E. STODDART, *ibid*. 13, 86), R. KAYSER (*ibid*. 15, 187), H. HAGER (Researches, 1, 163), A. CHRISTOMANOS (Zeitschr. f. anal. Chem. 17, 249), E. F. SMITH (*ibid*. 514), W. DITTMAR (*ibid*. 18, 126), F. FELS (*ibid*. 18, 498), W. J. SELL (Journ. Chem. Soc. 1879, p. 293).

I. Methods of Decomposition.

a. J. Blodget Britton's Method.—0·5 gram of the very finely powdered mineral is mixed as intimately as possible with 4 grams of a mixture of 1 part of chlorate of potassa and 3 parts of soda lime, and the whole heated to bright redness in a covered platinum crucible for at least an hour and a half. The unfused mass is easily removed from the crucible and powdered. The decomposition is complete. If the temperature is raised by employing the gas blowpipe, total decomposition is effected in twenty minutes (FELS). The melt contains all the chromium as alkaline chromate. The operation, a modification of CALVERT'S process (who employs nitrate of potassa instead of chlorate of potassa), is simple and effectual, and, as it can be performed in a platinum crucible, is strongly to be recommended.

b. Kayser's Method.—One part (about 0·5 gram) of the very finely powdered chrome iron ore is mixed with 2 parts of anhydrous carbonate of soda and 3 parts of slaked lime, and the mixture is kept at a bright red heat in an open platinum crucible for about an hour by means of the gas blowpipe and frequently stirred. The result is a sintered mass, from which the chromate of soda that has been formed is easily extracted with hot water. In a well-conducted operation, the residue does not contain any chromium.

c. Dittmar's Method.—2 parts of borax glass is melted with 3 parts of mixed carbonates of potash and soda, and this flux is kept in closed vessels. For the decomposition, 0·5 gram of the very finely powdered mineral is fused with 5 to 6 grams of the flux in a platinum crucible over a Bunsen burner. At first it is heated to redness for about five minutes with the crucible covered, then the crucible is uncovered, placed sloping over the flame, submitted to the greatest heat which the lamp can produce, the mixture being stirred with a platinum wire until the mineral is completely dissolved. To effect this the fusion is maintained with access of air for about three-quarters of an hour. By means of hot water all the chromium may be extracted from the fused mass in the state of alkaline chromate. If the Bunsen burner does not heat it to bright redness, the gas blowpipe must be employed if the decomposition is to be completed with certainty (FELS).

d. Christomanos' Method.—CHRISTOMANOS recommends, if the chromite has to be submitted to complete analysis, the method of PÉLIGOT and CLOUET slightly modified. 0·3 to 0·5 gram of the very finely powdered chrome iron ore is mixed most intimately with 3 to 3·5 grams of pure anhydrous carbonate of soda, and the mixture heated in a covered platinum dish for two hours over the gas blowpipe, so that it is kept in the fused state. (By the addition of a small quantity of nitrate of potassa, about 0·5 gram, the decomposition is certainly very much hastened, but the dish is strongly attacked; the addition of nitrate of potassa, therefore, is not to be recommended.) The decomposition is complete, but the heating for two hours over the gas blowpipe is inconvenient. The melt contains all the chromium as alkaline chromate.

e. For a simple determination of the amount of chromium, CHRISTO-

MANOS mixes intimately 0·3 to 0·5 gram of the chrome iron ore with 4 grams of thoroughly dried, and still warm, caustic soda, and 1·7 to 2 grams of calcined magnesia in a mortar, heats the mixture in a platinum, or preferably in a gold, crucible for an hour over a simple Bunsen burner and stirs frequently with a platinum wire. On boiling it with water, the chromium contained in the sintered mass readily passes into solution as chromate of soda.

f. Method of T. S. Hunt and F. A. Genth.—About 0·5 gram of the powdered ore is fused in a capacious platinum crucible with 6 grams of acid sulphate of potassa for fifteen minutes at a temperature scarcely exceeding the melting point of the latter, the heat is then slightly increased, so that the bottom of the crucible is just red-hot, and it is maintained at that temperature for about fifteen to twenty minutes. The melt must not rise higher than half-way up the crucible. The mass begins during this time to flow quietly, fumes of sulphuric acid escaping freely. After the lapse of twenty minutes the heat is increased, so that the second equivalent of sulphuric acid is driven off and the sulphates of iron and chromium are partially decomposed. 3 grams of pure carbonate of soda is then added to the fused mass, it is heated to fusion, and 3 grams of nitrate of potassa is added gradually in the course of an hour, during which it is maintained at a gentle red heat; it is then heated to bright redness for fifteen minutes. The melt contains the chromium as alkaline chromate. The operation is rather prolix, and attacks the platinum crucible; but it yields good results.

II. Methods of Analysis.

a. *Determination of all the Constituents.*

If all the constituents of the chrome iron ore are to be determined, it is best to employ one of the methods of decomposition in which alkaline salts alone are applied, preferably—in order to also avoid the presence of boric acid—method *d* or *f*. The cooled melt is treated with boiling water, filtered hot, and the undissolved portion is washed with boiling water. The residue is digested with warm hydrochloric acid. If any unattacked ore remains undissolved, this must not be weighed and deducted, but must be decomposed afresh. In the alkaline filtrate, which contains all the chromium as alkaline chromate, small quantities of manganic acid, silica, alumina, and occasionally titanic acid are found. To separate these, the solution is evaporated down with excess of nitrate of ammonia on a water bath, almost to dryness and until all the liberated ammonia is driven off. On adding water, silicic acid, titanic acid, alumina, and oxide of manganese remain undissolved. The solution is filtered and the filtrate is mixed with excess of sulphurous acid, to reduce the chromic acid to sesquioxide of chromium, heated cautiously to boiling, and pure ammonia free from silicic acid is added in slight excess, best in a platinum dish, or, if this is not to hand, in a porcelain dish; a glass vessel must not be used. The whole is then boiled for some minutes, and the separated hydrate of sesquioxide of chromium, washed by repeated boiling and decanting on a filter until the washings are free from sulphuric acid. After the precipitate has been dried and ignited, it will contain alkaline chromate, in consequence of the presence of a small quantity of alkali which the washing has failed to remove. Before weighing, therefore, it is boiled with water, a few drops of sulphurous acid added and then ammonia; it is again collected, washed, dried, ignited, and the pure oxide of chromium finally weighed (F. A. GENTH).*

The constituents of the hydrochloric acid solution, and also those separated by evaporation with nitrate of ammonia, are separated by the methods given in the General Part.

CHRISTOMANOS† has also thoroughly investigated the complete analysis of chrome iron ore. He advises the following method:—The melt is prepared according to I. *d*. When it is nearly cold the crucible, together with its contents and lid, is placed in a deep porcelain dish containing 300 to 400 c.c. of boiling water. The disintegration of the melt soon takes place. After about five minutes the crucible and lid are taken out; the small portions that adhere to it are rubbed off and carefully washed out with hot water. A small quantity of hydrochloric acid is then placed in the crucible and it is put aside for a time.

The contents of the porcelain dish are now boiled for five to ten minutes until the liquid, which at first is rusty brown, green, or bluish green from the presence of manganate and ferrate of soda, becomes pure deep yellow. As soon as this point is reached the liquid is filtered by means of a vacuum filter, the precipitate thoroughly washed with hot water and then, by drawing a rather strong current of air through it, dried sufficiently to allow of its being removed from the filter paper. It is then treated, together with the filter ash, with hydrochloric acid, the hydrochloric acid from the platinum crucible that has been put aside is added, and the whole evaporated to dryness on a water bath with the addition of a few drops of nitric acid; it is then moistened with hydrochloric acid, and evaporated to dryness, this operation being repeated several times; the residue is treated with hydrochloric acid and then with water, the silica removed and then the iron, lime and magnesia are separated by the methods given in the first volume. If the silica that has been obtained does not completely dissolve in a boiling solution of carbonate of soda, the residue—unattacked chrome iron ore—must be again decomposed.

In the *yellow solution* obtained by extracting the melt with water, the alumina present exists as aluminate of soda, and the chromium as chromate of soda, the solution may also contain silicate of soda and, in many cases, titanic acid. These are separated by the methods already given.

In the calculation and arrangement, the chromium should be put down as oxide of chromium, but the question is more difficult as regards the iron. As a rule it is all present as ferrous oxide; but in many chromites ferric oxide displaces part of the oxide of chromium. In that case the loss of weight, which the dry mineral sustains on prolonged heating in a current of hydrogen, can alone give information. Chromites, which contain peroxide of iron in the intermingled matrix, give this up on prolonged heating of the finely powdered mineral with hydrochloric acid. If lime is present, which usually occurs as carbonate, a carbonic acid determination is as a rule requisite. The chromite employed for this determination must naturally not be ignited.

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* Zeitschr. f. anal. Chem. 1, 498.

† *Ibid.* 17, 249.

b. Simple Determination of the Chromium in Chrome Iron Ore.

Since the value of a chrome iron ore depends merely on the amount of chromium it contains, it is frequently sufficient to determine this constituent only. In this case, as a rule, a gravimetric process is employed, one of the following methods being adopted.

a. The melt, which is best prepared according to I. *a.*, *b.* or *e.*, is thoroughly extracted with water, and the chromic acid is determined by § 130, I. *e. a.* in the solution, or an aliquot part of it after it has been warmed with an excess of sulphuric acid, so as to redissolve the precipitate of alumina, and again allowed to cool. If the solution contains no metallic chloride (Melt I. *b.* or *e.*), the excess of ferrous sulphate is most conveniently determined by permanganate of potassa (§ 112, 2, *a.*); if, on the other hand, it contains a metallic chloride (Melt I. *a.*), PENNY's method (§ 112, 2, *b.*) is to be preferred.

β. Melt I. *a.* is heated with a small quantity (about 20 c.c.) of water, and, after cooling, hydrochloric acid (15 c.c.) of about 1·12 sp. gr. is added. All should dissolve except the silica, which has separated out. A known quantity (§ 130, I. *e. a.*) of ferrous sulphate is now added in excess, and the excess is determined (J. BLODGET BRITTON). The determination of the excess of ferrous oxide by direct titration with permanganate of potassa, as BRITTON recommends, is inadmissible (see Vol. I. p. 219, *γ.*); PENNY's method (§ 112, 2, *b.*) must be employed for this purpose.

Melts prepared with the addition of alkaline nitrates cannot be examined by these methods, as they contain alkaline nitrites, and this acid would partly reduce the chromic acid on acidifying the aqueous solution of the melt.

11. ZINC COMPOUNDS.

A. Calamine: B. Electric Calamine.

§ 240.

The former of these ores consists of carbonate of zinc, which commonly contains larger or smaller admixtures of ferrous oxide, protoxide of manganese, oxide of lead, oxide of cadmium, lime, magnesia, and silicic acid, sometimes oxide of copper also; the latter consists of a hydrated basic silicate of zinc, which frequently contains admixtures of carbonate of zinc, also of ferrous and ferric oxides, and sometimes protoxide of manganese, oxide of lead, alumina, lime, and magnesia.

The ore is reduced to a fine powder, and analysed, either undried or dried at 100°. In the first case, a determination of the water must be made by drying a sample at 100°. The undried powder should be employed if the state of oxidation of the iron has to be accurately determined.

Determination of all the Constituents.

a. A portion of the powder is treated as directed in § 140, II. *a*, that is, the *silicic acid* is separated in the usual way. As the silicic acid generally contains *sand* or undecomposed *gangue*, it must be separated therefrom by boiling with a solution of carbonate of soda

(§ 237, 2, *b.*). In treating the residue with hydrochloric acid and water, 4 parts of acid of 1·1 sp. gr. are used to about 100 parts of water (§ 162, A. β.).

b. The solution obtained by this process is precipitated with sulphuretted hydrogen, and the *metals of the fifth and sixth groups*, which may be thrown down, are separated by the proper methods described in Section V. The current of sulphuretted hydrogen must not be passed for too long a time, as otherwise sulphide of zinc would be precipitated as well. In any case it is advisable to dissolve the precipitate of the metallic sulphides in hot hydrochloric acid, with the addition of a small quantity of hydrobromic acid, and, after the excess of bromine has been driven off, to again precipitate with sulphuretted hydrogen. In this second precipitation, care must be taken to add 4 parts of hydrochloric acid to each 100 parts of water (§ 162, A. β.).*

c. The filtrate (or filtrates) is neutralised with ammonia and then precipitated with sulphide of ammonium; the precipitate is treated exactly as directed in § 108, *b.*; the oxide of zinc obtained, which contains ferric oxide, sesquioxide of manganese and some silicic acid, is boiled with water, weighed, and the *manganese* determined volumetrically in a weighed portion of it (Vol. I. p. 449, **109**), the solution filtered from the undissolved silicic acid, which must be determined, and lastly, the ferric oxide is determined in the hydrochloric acid solution, with stannous chloride (Vol. I. p. 225). The *oxide of zinc* is estimated by difference. Of course one might employ any other of the methods given in § 160 for the estimation or separation of the zinc, manganese and iron contained in the sulphide of ammonium precipitate, but in none are accuracy and expedition so favourably combined. If, however, the amount of ferric or ferrous oxide is high, it is preferable to make a direct determination by the second method given in § 241.

d. The filtrate from the sulphide of zinc is acidified with hydrochloric acid, boiled for some time, the separated sulphur filtered off, and the *lime* and *magnesia* determined as directed in § 154, 6, (**36**).

e. A separate sample is ignited in the bulb-tube of the apparatus described in Vol. I. p. 56. The loss of weight in the bulb-tube indicates the water + carbonic acid; the increase of weight of the chloride of calcium tube gives the *water* alone; the difference shows the *carbonic acid.* In cases where the presence of a considerable proportion of ferrous oxide would impair the accuracy of this indirect estimation of the carbonic acid, or if the amount of carbonic acid is very small, one of the methods described in § 139, II. *e*, should be employed.

If the ore contains ferric oxide and ferrous oxide, these are determined by means of chromate of potassium in the hydrochloric acid solution prepared in a current of carbonic acid (Vol. I. p. 220, *b.*).

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* According to LARSEN (Zeitschr. f. anal. Chem. 17, 312), the double precipitation can be avoided if, on the first precipitation by sulphuretted hydrogen, there are 30 c.c. of hydrochloric acid of sp. gr. 1·10 in 250 c.c. of the solution (a proportion of hydrochloric acid which is suitable for the separation of zinc from copper, but not from cadmium), and the precipitate is first washed with hydrochloric acid of 1·05 sp. gr. saturated with sulphuretted hydrogen and then with sulphuretted hydrogen water.

C. Blende.

§ 241.

Zinc blende consists of sulphide of zinc, usually mixed with other sulphides, more especially those of lead, cadmium, copper, iron, and manganese. Small quantities of arsenic, antimony, nickel, and cobalt sometimes occur in the ore. Besides these, regard must be had in the analysis to the gangue mixed with the ore.

The ore is reduced to a very fine powder, which is dried at 100°.

Determination of all the Constituents.

First Method.

a. The *sulphur* is determined in one portion, best according to the method given in Vol. I. p. 383, 1, *a.*; it must not be forgotten that blende frequently contains lead.

b. The estimation of the *metals* is best made in another portion. For this purpose, 1 to 2 grams of the ore is heated with fuming hydrochloric acid until no more sulphuretted hydrogen escapes, some nitric acid is added, and 5 or 6 c.c. of pure concentrated sulphuric acid, previously diluted with a little water, and the whole evaporated until the hydrochloric and nitric acids are expelled. It is then diluted with 20 to 30 c.c. of water, and filtered. If the residue contains sulphate of lead—and this is usually the case—it is washed with water containing sulphuric acid, and then with spirit; the spirituous washings being collected separately.

The washed residue is repeatedly treated, at a boiling heat, with a solution of acetate of ammonia, until all the sulphate of lead is dissolved; the residual matrix is then ignited and weighed. The lead is precipitated from the solution in acetate of ammonia by sulphuretted hydrogen, and is determined as sulphate of lead (§ 116, 3).

The sulphuric acid solution is treated with hydrochloric acid of sp. gr. 1·1 in the proportion of 4 parts of acid to 100 c.c. of the solution, and the operation is proceeded with as in § 240, *b*. Blendes rich in iron are better examined by the second or third method, or the zinc may be separated as sulphide in presence of sulphocyanate of ammonia by a method recently published by ZIMMERMANN.*

For this purpose, the filtrate from the precipitate produced by sulphuretted hydrogen is evaporated almost to dryness on a water bath, diluted, and carbonate of soda cautiously added (at the last in rather dilute solution), until a slight permanent cloudiness is produced, and the solution is thus made as nearly as possible neutral; this is the condition necessary for success in ZIMMERMANN's method. An excess of a not too dilute solution of sulphocyanate of ammonia is now added, and the sides of the vessel (an Erlenmeyer's flask is the best for the purpose) are washed down with water; it is then warmed to from 60° to 70°, and a very moderate current of sulphuretted hydrogen is passed through it several times, but for not too long at a time, until the odour of the gas no longer disappears on exposing the solution to the air. At first the solution has merely a milk-white cloudiness; later on the sulphide of zinc separates completely, while the iron and manganese (also nickel and cobalt) remain dissolved. The precipitate is allowed to settle completely at a moderate temperature, collected, and the perfectly white precipitate is washed with water to which sulphuretted hydrogen water and solution of sulphocyanate of ammonia have been added; it is then dried, and the sulphide of zinc is ignited (Vol. I. p. 200, 2). Instead of this method of determination, another proposed by VOLHARD* may be employed. It consists in dissolving the sulphide of zinc in hydrochloric acid, evaporating the solution to dryness in a weighed platinum dish on a water bath, adding an excess of pure oxide of mercury free from alkali, and made into a cream with water, again evaporating to dryness and igniting. The oxide of zinc thus obtained is weighed.

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* Ann. der Chem. u. Pharm., 199, 1.

In the filtrate from the sulphide of zinc, the sulphocyanates are cautiously destroyed by heating with nitric acid, which is added in small quantities at a time (the operation must be performed in a capacious flask), and then—after filtration, if necessary—the iron is precipitated as basic salt (Vol. I. p. 437, 3, *a.*), and finally the manganese in the filtrate from this is precipitated by sulphide of ammonium.

Second Method (HAMPE †).

a. About 1 gram of the finely powdered mineral, dried at 100°, is boiled with nitric acid in a flask with a long neck. After all the nitrous acid has been driven off, and the solution is highly concentrated, 30 c.c. of nitric acid, sp. gr. 1·2, and about 200 c.c. of water are added.

b. The solution, without previous filtration, is precipitated by means of sulphuretted hydrogen, and without warming; after complete precipitation, the deposit is collected along with the undissolved gangue, washed, and treated on the filter with hot but not too concentrated nitric acid; the filter paper is pierced, all the undissolved substance is washed into a flask, the filter paper washed, and the liquid vigorously boiled; about 200 c.c. of water and 30 c.c. of nitric acid, sp. gr. 1·2, is now added and the solution again precipitated with sulphuretted hydrogen, filtered and the filtrate added to that first obtained.

c. The filtrates are boiled down in a long-necked flask almost to dryness, and the liquid, which is now free from sulphuretted hydrogen and contains all the iron as ferric salt, is, after cooling, saturated with ammonia, filtered, and the filter washed; the precipitate on the filter paper is again dissolved in hot, moderately strong nitric acid; again precipitated after cooling with excess of ammonia, filtered through the same filter paper, and this operation of dissolving in nitric acid and precipitating with ammonia is repeated once or twice. The precipitate consists principally of ferric oxide, but it may also contain alumina and sesquioxide of manganese, which are separated by § 161.

d. The ammoniacal solutions obtained in *c.* are acidified with acetic acid, diluted to at least 2 litres, and sulphuretted hydrogen is passed through them. They are then allowed to remain for at least 12, but preferably for 24 hours, when the clear liquid is poured off through the filter and the perfectly white sulphide of zinc is collected on it. On account of the extreme dilution, and because, in the analysis, neither hydrochloric acid nor non-volatile substances have been added, a short washing with sulphuretted hydrogen water, to which a small quantity of acetate of ammonia has been added, is sufficient. The dried sulphide of zinc, together with the filter ash, is melted in a Rose's crucible, with some pure sulphur and then treated according to § 108, 2.

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* *loc. cit.* p. 6.

† Zeitschr. f. anal. Chem. 17, 362.

e. To the filtrate from the sulphide of zinc, contained in a large flask, ammonia is added to alkaline reaction, then a small quantity of sulphide of ammonium, and the whole is left in a moderately warm place for at least 24 hours. A precipitate settles, which must be examined as to whether it still contains zinc; if the operation has been properly carried out this will not be the case. As a rule, the precipitate which is thus formed is sulphide of manganese.

f. The filter contents obtained in *b.* are treated with hydrochloric acid containing a small quantity of bromine, when the gangue remains undissolved and is dried and weighed. As a precaution it is tested to see whether on heating it with a solution of acetate of ammonia any sulphate of lead is dissolved.

g. The brominated hydrochloric acid solution obtained in *f.* is heated with ammonia in order to remove the excess of bromine, and the metals (lead, copper, cadmium, arsenic, and antimony) contained in the solution are then determined by methods §§ 163 & 164.

h. The determination of the sulphur is made by the first method.

Third Method (CLASSEN*) :—

The blende is heated with concentrated hydrochloric acid, and towards the end a small quantity of nitric acid is added; the excess of acid is then removed by evaporation, the residue extracted with hydrochloric acid and water, the gangue removed by filtration, and the metals of the fifth and sixth groups are precipitated by sulphuretted hydrogen (see § 240, *a.* and *b.*). The filtrate and washings are evaporated, with the addition of nitric acid or bromine water towards the end, so as to ensure that all the iron is present as ferric oxide or the corresponding chloride. The excess of acid is removed by evaporation on the water bath, and when cold 10 c.c. of bromine water is added and the mixture digested for some time on a water bath.

A solution of neutral oxalate of potassa (1 : 3) equal to about seven times the amount of the oxides present is now added, the solution warmed for about a quarter of an hour on a water bath, and any residue of basic ferric salt which may remain undissolved is brought into solution by adding acetic acid, drop by drop. If the amount of oxalate of potassa which has been added is sufficient, a perfectly clear solution is obtained, coloured more or less green; if, on the other hand, the amount of oxalate of potassa is insufficient for the formation of oxalate of potassa and ferric oxide and oxalate of potassa and zinc, the liquid is rendered opaque by oxalate of zinc; in the latter case oxalate of potassa must be added until a clear solution is obtained. The solution is now heated to boiling and decomposed with concentrated acetic acid of about 80 per cent., with continuous stirring. The amount of acetic acid must be at least equal in volume to the liquid to be precipitated. By this means all the zinc separates out as heavy crystalline oxalate of zinc, while the iron remains dissolved. The well-covered beaker is heated for about six hours at about 50°, the solution filtered hot, and the precipitate thoroughly washed with a mixture of equal volumes of concentrated acetic acid, alcohol, and water; it is then dried, the filter paper burnt first on a platinum wire, and the precipitate heated in a covered platinum crucible, at first very gently, gradually raising the temperature; it is finally ignited with access of air and weighed. The ignited residue is now warmed with water, and the reaction tested; if it is alkaline, the carbonate of potassa, which is still present, is removed by washing, and it is re-weighed.

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* Zeitschr. f. anal. Chem. 16, 471 ; 18, 190, 381, 397.

If the mineral contains manganese, the oxide of zinc may contain the whole of it as oxide of manganese. If the quantity is weighable, it is determined according to Vol. I. p. 449, *d.* The weight of the oxide of zinc is given by the difference.

The iron may be precipitated by adding ammonia to the filtrate from the oxalate of zinc. The determination of the sulphur is made as in the first method.

The comparative analyses communicated by CLASSEN yielded very concordant results. The author is personally insufficiently acquainted with the method to be able to give a decisive opinion on it.

D. Zinc Ores in general.

I. Volumetric Estimation of Zinc.

§ 242.

As the gravimetric methods for the estimation of zinc take much time, volumetric methods are employed almost exclusively in zinc works, as these give results which are sufficiently accurate for most purposes, and can be carried out comparatively rapidly.

a. Method with Sulphide of Sodium.

This method, which was originally proposed by SCHAFFNER,* has been the subject of a variety of modifications. These are described in the papers mentioned below.† The following has been found to be the best method.

α. Method with SCHAFFNER'S *modified End Reaction.*

1. Preparation and standardizing of the solutions.

Sulphide of Sodium Solution.—This is prepared either by dissolving crystallised sulphide of sodium in water (about 100 grams to 1000–1200 water), or by supersaturating a solution of soda, free from carbonic acid, with sulphuretted hydrogen, and subsequently heating the solution in a flask to expel the excess of sulphuretted hydrogen. Whichever way it is prepared the solution is afterwards diluted, so that 1 c.c. may precipitate about 0·01 gram of zinc.

Solution of Zinc.—A solution of zinc is prepared by dissolving 10 grams of chemically pure zinc, or 12·459 grams of pure oxide of zinc, in hydrochloric acid, or 44·122 grams of dry crystallized sulphate of zinc in water, or 68·133 grams of dry crystallised sulphate of potash and zinc in water, and making the solution in either case up to 1 litre with water. Each c.c. of this solution corresponds with 0·01 gram of zinc.

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* Journ. f. prakt. Chem. 73, 410.

† C. KUNZEL (Journ. f. prakt. Chem. 88, 486); C. GROLL (Zeitschr. f. anal. Chem. 1, 21); STADLER (*Ibid.* 4, 213 and 468); DEUS (*Ibid.* 9, 465); SCHOTT (*Ibid.* 10, 209); LAUS (Berg- und Hultenmann. Zeitung, 35, 148, 173); THUN (*Ibid.* 35, 225); TOBLER (*Ibid.* 35, 304, and Zeitschr. f. anal. Chem. 17, 357); W. HAMPE and FRAATZ (*Ibid.* 17, 359).

Hydrated Oxide of Iron.—Three grams of iron wire are dissolved by the aid of heat in hydrochloric acid, the ferrous chloride is then converted into ferric chloride by boiling with a small quantity of nitric acid, and the solution is diluted to 100 c.c. Shortly before using, 1 to 2 drops of the solution are added to 1 c.c. of undiluted aqueous ammonia, the same number of drops being always taken; every drop produces a ring of hydrated oxide of iron until the exact moment of reaching the desired maximum of opacity. After the lapse of about a minute the hydrated oxide of iron suspended in ammonia is fit for use (THUM).

2. Solution of the ore and preparation of the Ammoniacal Zinc solution.

In the case of rich ores 1 gram, in the case of poor ones 2 grams of the finely powdered ore,* either air-dried or dried at 100°, is put into a small flask, warmed with hydrochloric acid, to which some nitric acid is added, and the excess of acid expelled by evaporation. If lead is present it is separated by evaporating the solution with some sulphuric acid, taking up the residue with water and filtering. Other metals of the fifth and sixth groups, if present, are precipitated with sulphuretted hydrogen (see § 240, *a.* and *b.*).

The solution, which does not contain, or no longer contains, metals of the fifth and sixth groups is boiled, if necessary, with nitric acid, in order to convert all the iron into ferric oxide or chloride; a small quantity of hydrobromic acid is added if manganese is present, and it is diluted with water. Ammonia solution is then added to the cold liquid in excess, and the precipitate, which consists principally of hydrated oxide of iron, is collected on a filter. If the amount is small, it is washed with lukewarm water and aqueous ammonia until a white turbidity consisting of sulphide of zinc is no longer produced in the washings on adding sulphide of ammonium or sulphide of sodium to them; for in this case the amount of zinc which is contained in, and cannot be washed out of, the hydrated oxide of iron (which, according to HAMPE and FRAATZ, is approximately one-fifth of the weight of the iron present) may as a rule be ignored.

If, however, the precipitate of hydrated oxide of iron is considerable, the moderately washed oxide is dissolved in hydrochloric acid and again precipitated as basic salt, preferably according to § 160, 3, *a.*, or by Method 4. The solution which is filtered from it is concentrated by evaporation, decomposed with excess of ammonia, filtered, if necessary, added to the principal solution and made up to 1 litre. If the zinc ore contains an appreciable amount of manganese, the liquid which has been separated from the basic ferric salt, and concentrated by evaporation, is decomposed by hydrobromic acid before ammonia is added in excess; after the lapse of a considerable time, the precipitate of hydrated peroxide of manganese is collected (all these precipitates of hydrated peroxide of manganese, or those produced in a similar manner, retain a small quantity of zinc), and the solution is made up to 1 litre.

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* If the ore contains organic matter this must be destroyed by gentle ignition.

3. Titration of the Solution.

To 500 c.c. of the ammoniacal zinc solution, hydrated oxide of iron (see above) suspended in ammonia is added, and then from a burette solution of sulphide of sodium, until the greater part of the hydrated oxide of iron, which has collected on the sides of the beaker, has become brown or black (it is necessary to select one of these tints once for all), and the amount is read off. A quantity of zinc solution of known composition approximately corresponding with the sulphide of sodium solution employed is then measured off, treated with ammonia in excess, diluted with water so that the volume is as nearly as possible equal to the original titrated solution, an equal quantity of hydrated oxide of iron suspended in ammonia is added, and then solution of sulphide of sodium is allowed to run in until the colour of the hydrated oxide of iron—after an equal interval—shows the same tint of brown or black that it did in the first titration. If, in this determination, the final reaction is not considered sufficiently decisive, the other half litre is available for a repetition of the experiment.

The relation of the sulphide of sodium solution to the zinc solution of known composition is thus obtained accurately, as it has already been to that of unknown composition, and therefore the amount of zinc contained in the solution of the mineral may be easily calculated.

A correction for the amount of sulphide of sodium necessary to blacken the hydrated oxide of iron is not required, because the titration is effected under precisely similar circumstances in both cases, and the solutions employed contain almost identical amounts of zinc (THUM; HAMPE). But even when all these precautions are taken, the results obtained by means of this method are only accurate within 0·5 per cent. (HAMPE).

BARRESWIL,* instead of the flocks of ferric oxide, employs small fragments of ignited porcelain, which are moistened with ferric oxide and then thrown into the ammoniacal zinc solution.

β. *The Künzel-Groll End Reaction.*

1. Materials required.

Sodium sulphide solution and zinc solution of known strength, as in *a*. Also pure dilute solution of nickel chloride.

2. Method employed.

The dissolution of the ore, and the making up of the zinc to 1 litre of an ammoniacal solution free from any of the other heavy metals is carried out as in *a*.

To 500 c.c. of this solution, sulphide of sodium is run in from a burette as long as a distinct precipitate continues to be formed, stirring briskly; a drop of the liquid is taken out by a glass rod, transferred to a porcelain plate, spread out so that it may cover a somewhat large surface, and in the middle a drop of pure dilute solution of chloride of nickel is put. If the whole of the zinc is not precipitated, the edge of the drop of nickel solution remains blue or green, and more sulphide of sodium must be added, testing from time to time, until at last a blackish grey coloration appears surrounding the nickel solution. The reaction is now completed, the whole of the zinc is precipitated, and a slight excess of sulphide of sodium has been added. The precise depth of colour of the nickel must be carefully observed and remembered, as it will have to serve as the criterion for stopping in future experiments. To make sure that all the zinc is precipitated, a few tenths of a c.c. more of the reagent may be added and the test again applied, when of course the colour of the nickel-drop should be darker. The number of c.c. used is noted, and the experiment repeated with the remaining 500 c.c. of the ammoniacal solution, running in at once the necessary quantity of the reagent, *less* 1 c.c., and then adding 0·2 c.c. at a time until the end reaction is reached. The last experiment is taken as giving the correct result.

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* Journ. de Pharm. 1857, p. 431; Polytech. Centralbl. 1858, p. 285.

An amount of the zinc solution of known strength corresponding with the sodium sulphide solution used in the last experiment is now measured out, ammonia is added in excess, and then water until the volume of the liquid is about the same as that of the solution first titrated; the sodium sulphide solution is now run in until the end reaction is reached. In this way the relation of the sodium sulphide solution to the zinc solution of known and unknown strengths is determined, and from this the amount of zinc in the ore can be easily calculated.

According to C. Künzel, the error when this method is carefully worked does not exceed 0·5 per cent.

With respect to other reactions for detecting small quantities of sodium sulphide in the precipitated zinc solution, the following may be noticed.

Deus in his criticism of the end reactions arrives at the conclusion that filter paper moistened with cobalt chloride solution and again dried (0·27 gram cobalt in 100 c.c. of the solution) gives the most certain indication. The paper, when a spot of the liquid containing the suspended zinc sulphide is placed on it, shows a white spot with pale-blue edge. Directly, however, there is the slightest excess of sodium sulphide, a sharply defined dark coloration appears within the white ring.

The formation of sulphide of lead is often employed to indicate the end reaction, and the author prefers the following method, which he proposed long ago,* to all others:—A piece of white filter paper, moistened with solution of acetate of lead, is placed on a layer of blotting paper, some carbonate of ammonia dropped on to it, so as to form a thin coating of carbonate of lead, and, when the blotting paper has absorbed the excess of moisture, the lead paper is spread on a porcelain plate. As soon as the zinc seems to be nearly all precipitated, a small piece of filter paper is laid on the lead paper, and then the end of a blunt glass rod is dipped in the liquid, and pressed somewhat gently on the small piece of filter paper. As long as the sulphide of sodium is not in excess, no brown stain is formed, but directly it begins to be in excess, a brown spot appears on the lead paper.

Schott employs glazed paper covered with a coating of white lead which is known in Germany as "Polkapapier," and is employed for visiting cards. If a drop of the liquid containing the suspended zinc sulphide is taken out with a glass rod and allowed to flow back into the beaker, over a strip of the glazed lead paper, there is no discoloration of the paper; but directly excess of sodium sulphide is present, a brown ring is formed where the liquid has flowed between the end of the rod and the paper.

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* Quant. Chem. Anal., 5th German edition, p. 814.

b. Potassium ferrocyanide Method.

GALLETTI* was the first to employ potassium ferrocyanide for the estimation of zinc volumetrically. He precipitated in an acetic acid solution at 40°; the milky appearance which the liquid assumes when there is excess of ferrocyanide of potassium present serving to distinguish the end reaction. He dissolves 32·485 grams of crystallised ferrocyanide of potassium to a litre, and reckons that 100 c.c. of this precipitates 1 gram of zinc. As, however, the precipitate is not pure zinc ferrocyanide, as he supposed, but ferrocyanide of zinc and potassium (REINDEL †), this is incorrect. In more recent communications, GALLETTI ‡ has modified the original method as regards the separation of iron. VON RENARD § has altered the method in so far as he adds excess of solution of potassium ferrocyanide to the ammoniacal zinc solution, makes up to a known volume, filters an aliquot part, and then determines the excess of potassium ferrocyanide by means of potassium permanganate (Vol. I. p. 378, *g.*), after adding a large excess of hydrochloric acid (30 c.c. hydrochloric acid to 100 c.c. of the solution). In this way the amount of potassium ferrocyanide employed for the precipitation of the zinc is estimated, and the quantity of the latter can be calculated from it.

C. FAHLBERG,‖ however, has devised the simplest form of the ferrocyanide method.

He employs a solution of potassium ferrocyanide of such a strength that 1 c.c. precipitates 0·01 gram of zinc. A zinc solution of known strength is prepared by dissolving 10 grams of pure zinc in hydrochloric acid, adding 50 grams of ammonium chloride and making up to 1 litre. The addition of ammonium chloride is advantageous, because, when it is present, the precipitate produced by potassium ferrocyanide is flocculent and contains no potassium ferrocyanide.

In order to determine the value of the potassium ferrocyanide solution, prepared by dissolving 46 to 48 grams of potassium ferrocyanide in 1000 c.c., a burette is filled with the zinc solution, and a second with the potassium ferrocyanide solution; 50 c.c. of the zinc solution is run into a beaker, 10 to 15 c.c. of hydrochloric acid, sp. gr. 1·12, added, and then 450 c.c. of water. The potassium ferrocyanide solution, in quantities of 1 to 2 c.c. at a time, is now run in with constant stirring until a drop of the liquid, mixed with a drop of uranium nitrate solution on a porcelain plate, shows a permanent brownish-red spot. More zinc solution is then cautiously run in until this reaction again disappears, and lastly the potassium ferrocyanide solution drop by drop, until it again appears. If, for example, 48 c.c. of the ferrocyanide solution are required for 51 c.c. of the zinc solution, the former must be diluted by the addition of 3 c.c. of water to every 48 c.c.

The solution of the ore is prepared as already described. After

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[*] Zeitschr. f. anal. Chem. 4, 213.

[†] *Ibid.* 8, 460; Neues Handwörterbuch der Chemie, p. 3, 244.

[‡] Zeitschr. f. anal. Chem. 8, 135, and 14, 190.

[§] *Ibid.* 8, 459.

[‖] *Ibid.* 13, 379.

removing the metals of the fifth and sixth group and the iron, 500 c.c. of the ammoniacal solution is neutralised with hydrochloric acid, 10 to 15 c.c. of hydrochloric acid sp. gr. 1·12 added, and the solution titrated with the potassium ferrocyanide solution, taking no notice as to whether manganese is present or not. The circumstance, that titrating in a liquid strongly acidified with hydrochloric acid (in which manganese ferrocyanide is soluble), renders it unnecessary to remove the manganese, makes FAHLBERG's the most convenient of the various modifications of the potassium ferrocyanide methods. As regards accuracy, the difference never exceeds 0·5 per cent.

c. C. MANN'S *Method.**

This method, which, although it involves more operations than those previously described, yields more accurate results, is founded on the fact that hydrated zinc and moist silver chloride easily and completely react, yielding silver sulphide and zinc chloride. By estimating the chlorine in solution, therefore, the amount of zinc is easily ascertained.

1. Materials required.

Well-washed moist *silver chloride.* This must be kept under water and protected from the action of light.

Solution of silver nitrate, which in 1 c.c. contains 0·03318 gram of silver corresponding with 0·01 gram of zinc. This is prepared by dissolving 33·18 grams of pure silver in nitric acid, boiling off the nitrous acid, and diluting the solution to 1 litre.

Solution of *ammonium sulphocyanate*, 3 c.c. of which precipitate 1 c.c. of the silver solution.

A cold saturated solution of *iron ammonia alum.*

2. Method employed.

0·5 to 1 gram of the ore is dissolved in nitric acid, the metals of the fifth group separated by sulphuretted hydrogen, and the iron and alumina by two precipitations with ammonia. The united filtrates are acidified with acetic acid, and sulphuretted hydrogen is passed into the liquid until the zinc is completely precipitated; the excess of sulphuretted hydrogen is then removed by brisk ebullition until a drop of the filtered liquid no longer colours lead paper, the liquid allowed to settle, decanted hot, the precipitate collected, and the unwashed zinc sulphide, together with the filter, transferred to a small beaker; 30 to 50 c.c. of hot water is then added, the mixture stirred and silver chloride in excess added, the whole boiled until the supernatant liquid is clear, and lastly 5 or 6 drops of dilute sulphuric acid (1 : 6) is added to the boiling solution. In this way, the zinc sulphide is completely converted into zinc chloride in the space of a few minutes.

The precipitate of silver sulphide and chloride is then separated by filtration, washed well, and the chlorine in the filtrate determined by VOLHARD's method.† For this purpose, to the zinc chloride solution, which should be about 200 to 300 c.c., 5 c.c. of the iron alum solution is added, and sufficient nitric acid to cause the colour of the ferric salt to disappear, then a measured quantity of the silver solution, somewhat more than enough to precipitate all the chlorine. The ammonium sulphocyanate solution is now run in drop by drop from a second burette, without previously separating the silver chloride or causing it to aggregate by shaking or boiling. The liquid must be continually swirled round, so that each drop as it falls in may rapidly mix with it. Directly the liquid acquires a pale brownish-yellow colour, which remains for about ten minutes after the mixture has been shaken round, the precipitation of the silver is complete. The number of cubic centimetres of silver solution corresponding with the ammonium sulphocyanate solution employed, is subtracted from the total silver solution added, and the difference gives the amount of zinc, reckoning 0·01 gram of zinc for each cubic centimetre of the silver solution.

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* Zeitschr. f. anal. Chem. 18, 162.

† *Ibid.* 18, 272.

The analyses quoted by MANN are in the highest degree satisfactory, and excellent results have also been obtained in the author's laboratory by this method.

J. B. SCHOBER'S* method of estimating zinc is also founded on VOLHARD'S process for silver estimation. The zinc is precipitated by sodium sulphide solution, the excess of the latter decomposed by silver solution, and lastly the excess of this determined by means of ammonium sulphocyanate. The method is too circuitous, and is not likely to come into general use.

II. Electrolytic Estimation of Zinc in Zinc Ores.

§ 243.

Numerous processes are given for the precipitation of zinc electrolytically.† From these it will be seen that the electrolytic precipitation of zinc can be effected without difficulty. The different experimenters, however, are not agreed as to which is the best method.

PARODI and MASCAZZINI ‡ at first proposed precipitation from a solution of the sulphate to which an excess of acetate of ammonia had been added; subsequently § they recommended the following. The zinc (0·1 to 0·25 gram) is dissolved as sulphate, 4 c.c. of a solution of acetate of ammonia (naturally a rather concentrated solution) is added, then 2 c.c. of a solution of citric acid (also concentrated), and the whole diluted to 200 c.c. The electrodes || are introduced so that they are only a few millimetres asunder, and the circuit closed; the platinum cone must be the negative electrode. The beaker must be covered with a properly arranged glass plate. The current of the Clamond thermopile must be strong enough to give off 250 to 300 c.c. of oxyhydrogen mixture per hour. As soon as a sample of the liquid no longer becomes turbid on the addition of ferrocyanide of potassium, the separation of the zinc is complete. The liquid is removed by means of a syphon, the cone washed with water, and the current stopped. The cone with the adhering zinc is finally washed twice with absolute alcohol, dried at 40° to 50° in a current of air, and weighed.

If the ore contains lead, cadmium, iron, &c., these metals must be previously removed by the method described in § 242.

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* Zeitschr. f. anal. Chem. 18, 467.

† See Zeitschr. f. anal. Chem. 8, 24; 15, 303; 16, 469; 17, 216; 18, 587; 18, 588.

‡ Zeitschr. f. anal. Chem. 16, 469.

§ *Ibid.* 18, 587.

|| As the electrolytic method is particularly important in the estimation of copper, the details of the method will be given under the analyses of copper compounds.

A. RICHE* adds ammonia to the solution of the zinc ore in nitric or sulphuric acid, from which the other metals have been previously removed, until the precipitate of hydrated oxide of zinc at first produced is completely dissolved, adds acetic acid in excess, and submits the solution to electrolysis. The deposited zinc adheres firmly to the platinum cone.

F. BEILSTEIN and L. JAWEIN † add soda to the solution of sulphate of zinc obtained from the zinc ore by the methods previously described until a precipitate is produced, and then cyanide of potassium until it re-dissolves to a clear solution. A current from four Bunsen elements is employed. If the liquid becomes warm, the beaker is placed in cold water. When the precipitation is supposed to be complete, the electrodes are removed from the liquids, the cone washed successively with water, alcohol, and ether, dried first in a desiccator, then at 100°, and weighed. The zinc is then dissolved off by hydrochloric or nitric acid, the cone washed and weighed, and the electrodes again introduced into the solution to see if there is any further deposit of zinc.

E. Metallic Zinc.

§ 244.

Metallic zinc as obtained in the metallurgical extraction of the metal contains various impurities. Many chemists have investigated these, especially C. W. ELIOT and F. H. STORER,‡ who have most carefully examined ten kinds of zinc (German, English, French, Belgian, and American).

The following are the most important results of their investigations:—

Almost all zincs (nine out of the ten kinds) contain lead varying in amount from 0·079 to 1·66 per cent. They all contain small quantities of cadmium; the amount of oxide of cadmium, which in many zincs contains small quantities of oxide of tin, varies from 0·0035 to 0·4471 per 100 parts of zinc. They all contain iron, in quantity varying from 0·0549 to 0·2088 per cent. Copper was found in one sample only. Arsenic does not occur so frequently as is usually believed; not a few zincs are free from it, others contain traces, many notable quantities. Of other metals, *nickel, cobalt*, and *manganese*, are found but exceptionally, and only in extremely minute quantities. Neither *carbon* nor *silicon* are found in zinc as a rule, but only traces occasionally. *Sulphur* is always present, but only in minute traces. ELIOT and STORER did not extend their investigations to *phosphorus*, traces of which are found in zinc.

Under ordinary circumstances it is only necessary to determine the lead, iron, and cadmium quantitatively; it is sufficient to test qualitatively for the other impurities.

The analysis is conducted as follows:—

1. 30 grams of the zinc, either granulated, or cut into small pieces if sheet-zinc, is treated with dilute sulphuric acid (1 part concentrated acid to 4 parts of water), warming gently. When the zinc is almost

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* Zeitschr. f. anal. Chem. 17, 216.

† *Ibid.* 18, 588.

‡ Memoirs of the Amer. Acad. of Arts and Sciences, new series, 8, pp. 57–94.

entirely dissolved, the zinc solution is poured off or filtered from the undissolved black residue; the latter is washed, dissolved in a little nitric acid (if this leaves any residue, it must be tested for tin), and the solution evaporated with a little dilute sulphuric acid until all the nitric acid is driven off. The residue is then again treated with the same dilute sulphuric acid, &c., and the separated sulphate of *lead* determined as in § 116, 3, *a*, *β*.

2. The filtrate from the sulphate of lead is diluted with water, 4 c.c. of hydrochloric acid sp. gr. 1·12 added for each 100 c.c., and sulphuretted hydrogen passed through the solution for fifteen minutes to precipitate the cadmium and any traces of tin or copper which may be present. As part of the cadmium, &c., may also be in the main zinc solution, this is also treated for fifteen minutes with sulphuretted hydrogen after dilution and addition of 4 c.c. of hydrochloric acid to each 100 c.c. of liquid. If a precipitate is produced, this is collected on the same filter as that employed for collecting the first precipitate of cadmium sulphide, &c. After washing, the contents of the filter are dissolved in 2 c.c. of brominated hydrochloric acid, 2 c.c. of hydrochloric acid added, and the whole diluted with 100 c.c. of water; the bromine is then driven off by heating, and the solution again precipitated with sulphuretted hydrogen. The precipitate is collected, washed and dried; the filter is then saturated with a concentrated solution of nitrate of ammonium, again dried and incinerated, the residue heated with a little sulphuric acid, evaporated, and the salts weighed as sulphates (§ 121, 3). If the residue dissolves in water on the addition of a slight excess of ammonia yielding a clear colourless solution, which gives a yellow precipitate with sulphide of ammonium, the weighed sulphate may be at once calculated as pure *cadmium* sulphate; if, however, the ammoniacal solution is blue, the cadmium oxide and *copper oxide* must be separated (§ 163). If there is an insoluble residue left on treating the sulphates with water and ammonia, this must be tested for tin.

3. In order to determine the *iron*, it is best to dissolve a fresh quantity of zinc, at least 10 grams, in pure dilute sulphuric acid (in the apparatus, Vol. I. p. 216, fig. 80), pour the cooled solution into a beaker, repeatedly wash the spongy lead which remains, and determine the iron which is present in the solution as ferrous sulphate, by means of a dilute solution of permanganate of potassium as in Vol. I. p. 218, *β*.

The qualitative detection of *arsenic* is best effected by means of Otto's modification of Marsh's process * using absolutely pure sulphuric acid. The presence of *sulphur* is most easily discovered by dissolving the zinc in hydrochloric acid, and testing the evolved gas with an alkaline lead solution or with lead paper. It is, however, necessary to take the greatest care in choosing the acid, for if this contains traces of sulphurous acid, it is self-evident that, even if the zinc is free from sulphur, the lead test will be blackened; if, on the other hand, it contains chlorine, no sulphuretted hydrogen will be formed, although the zinc may contain sulphur. Eliot and Storer † found these conditions so difficult to fulfil with hydrochloric acid prepared in the ordinary way, that they obtained the acid required by decomposing a solution of pure calcium chloride with pure oxalic acid.

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* See Qualitative Analysis, 10th edition, p. 171.

† *loc. cit.* p. 72.

The presence of *phosphorus* in zinc is best detected by the coloration of the hydrogen flame obtained when the zinc is treated with dilute sulphuric acid.*

F. Zinc-Dust.

§ 245.

The zinc-dust of commerce, consisting of finely divided zinc (more or less pure) intimately mixed with oxide of zinc, is valued not according to the total amount of zinc present, but according to the zinc present in the metallic state, since it is used almost exclusively as a reducing agent.

The two following methods are employed in the author's laboratory for ascertaining the value of zinc-dust.

First Method.†

According to this method, the zinc-dust is dissolved in dilute sulphuric or hydrochloric acid, the evolved hydrogen is burnt and the water thus formed is weighed, 1 equiv. of zinc being calculated for each equiv. of water.

The apparatus used for this purpose is the following:—To dissolve the gas, a flask of about 100 c.c. capacity is employed, furnished with a safety tube to introduce the acid, and a screw pinch-cock as shown in fig. 97, this vol., p. 234. The hydrogen evolved passes through a small refrigerating apparatus, likewise shown in the figure, to remove water. The gas is then passed into a U-shaped tube *a*, fig. 98, two-thirds filled with fragments of glass and containing 12 c.c. of pure concentrated sulphuric acid; *b c* is a combustion tube 340 mm. long. At the end towards *b* it contains, between two plugs of copper gauze, a layer of asbestos 120 mm. long, which has been ignited first in moist and then in dry air; the rest of the tube is filled with ignited granular oxide of copper, which is kept together at *c* by a plug of copper gauze or asbestos;

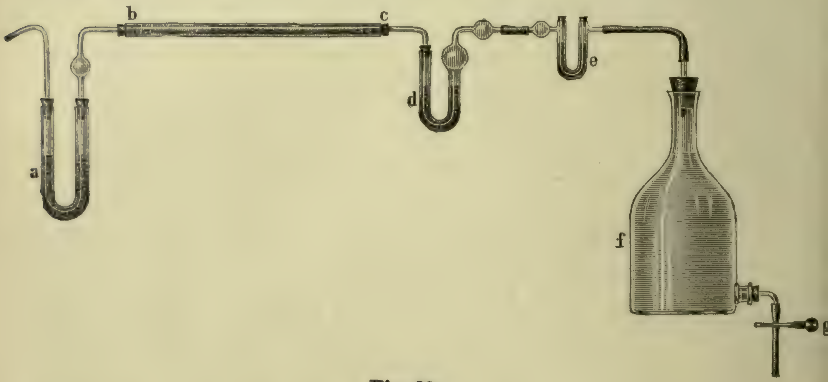

Fig. 98.

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* See Qualitative Analysis, 10th edition, p. 384.

† "Ueber die Werthbestimmung des Zinkstaubes," R. Fresenius, Zeitschr. f. anal. Chem. 17, 465.

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d is a **U**-shaped tube, half filled with fragments of glass and containing 6 c.c. of pure concentrated sulphuric acid,* *e* is a protecting tube containing chloride of calcium, and *f* is an aspirator.

The apparatus is arranged as shown in the figure, except that the tube *b c* is connected directly with the aspirator (that is, without *d* and *e*), the screw pinch-cock of the safety tube of the gas evolution flask opened a little, and a current of air drawn through the apparatus by opening the pinch-cock; the tube *b c* is then heated to redness throughout its entire length, and allowed to cool in a current of dry air. In the meantime, a weighed quantity of the zinc-dust (about 3 grams) is introduced into the gas evolution flask, and a little water added; the tube *d* is weighed, *g* is closed, and the apparatus rearranged as in the figure; the screw pinch-cock at the safety tube closed, and *g* opened again to ascertain that the apparatus is tight.

The tube *b c* where it contains the oxide of copper is now heated to redness, the pinch-cock at the safety tube opened somewhat, and dilute sulphuric acid to which a drop of chloride of platinum has been added, poured into the funnel *m*, allowing it to flow into the gas evolution flask. The screw pinch-cock at the safety tube is opened wide enough to allow single air bubbles to pass slowly through the acid which closes the lower bend of the safety tube. The evolution of hydrogen goes on steadily, more acid, without the addition of chloride of platinum, being allowed to run in from time to time until all the zinc is dissolved. The operation, which takes about an hour, may be facilitated by warming gently. The hydrogen mixed with excess of air, after being completely dried in *a*, is burnt to water in *b c*, without the copper oxide being permanently reduced, and this water is absorbed in *d*. Towards the end, the evolution flask is heated moderately so as to drive out the hydrogen dissolved in the liquid in it. When cold, the increase of weight in *d* is ascertained, and 32·53 parts of metallic zinc calculated for every 9 of water. The apparatus is then ready for a fresh determination, after renewal of the sulphuric acid in *a* and *d*.

Second Method (DREWSON).†

This is founded on the following reaction:—When zinc-dust is brought into contact with a sufficient quantity of dichromate of potassa and dilute sulphuric acid, there is no evolution of hydrogen, but the chromic acid set free by the sulphuric acid is reduced to oxide of chromium: $2CrO_3 + 3H = Cr_2O_3 + 3HO$.

It is requisite to have:—

a. A solution of dichromate of potassa, the strength of which is accurately known. This is prepared by dissolving 40 grams of the pure fused salt, and making up to 1 litre.

b. A solution of ferrous sulphate containing about 200 grams in the litre; it must be strongly acidified with sulphuric acid to retard oxidation.

It is necessary first to compare these two solutions, and for this purpose 20 c.c. of the ferrous solution is placed in a beaker, some sulphuric acid and about 50 c.c. of water added, and the solution of dichromate of potassa allowed to run in from a burette until a drop of the iron solution is no longer coloured blue by ferricyanide of potassium (Vol. I. p. 220, *b.*).

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* Instead of this tube, A. SCHRÖTTER'S sulphuric acid tube can of course be used as described in this vol., p. 33.

† Zeitschr. f. anal. Chem. 19, 50.

A weighed quantity of the zinc-dust (about 0·5 gram) is now placed in a beaker, together with 50 c.c. of the solution of dichromate of potassa, 5 c.c. of dilute sulphuric acid added and the whole well shaken; 5 c.c. more of dilute acid is then added, and the mixture allowed to stand a quarter of an hour with frequent agitation.

When all is dissolved, except the small residue which always remains, excess of sulphuric acid is added together with 100 c.c. of water and 25 c.c. of the ferrous sulphate solution, so as to reduce the greater part of the excess of chromic acid; more of the ferrous solution is then run in, about 1 c.c. at a time, until a drop of the solution gives a distinct blue colour with ferricyanide of potassium, finally titrating back with the dichromate solution until the blue colour no longer appears.

The number of cubic centimetres of the dichromate of potassa solution corresponding with the ferrous sulphate solution employed is deducted from the total dichromate solution taken, and the amount of dichromate of potassa in the difference multiplied by 0·66113 gives the metallic zinc in the zinc-dust.

12. MANGANESE COMPOUNDS.

A. Black Oxide of Manganese.

§ 246.

The native black oxide of manganese is a mixture of peroxide of manganese with the lower oxides of manganese, ferric oxide, clay, &c.; besides these impurities, it always contains moisture, and frequently chemically combined water. Now, as the commercial value of the article depends entirely on the amount of pure peroxide (or, more correctly, of available oxygen, expressed as peroxide of manganese) which it contains, it is a matter of the greatest interest for the manufacturer to ascertain this. By "available oxygen" is meant the excess of oxygen contained in a manganese over the 1 eq. corresponding with the protoxide of manganese, as on treating the ore with hydrochloric acid, an amount of chlorine is obtained equivalent to this excess of oxygen; 1 eq. of this available oxygen corresponds with 1 eq. peroxide of manganese, since $MnO_2 = MnO + O$.

Some years ago DE VRY* called attention to the importance of the question not only of drying the sample to be analysed, but also as to the way in which this operation is carried out, and the author has subsequently bestowed particular attention on this subject as it may give rise to considerable differences. On this account, a detailed account of the method of drying the sample is given before describing the actual methods of analysis.

I. Drying the Sample.

As all analyses of manganese proceed on the supposition that the sample operated on is a fair average specimen of the ore, a portion of a tolerably finely powdered average sample is generally sent for analysis to the chemist; in the case of new lodes, however, a number of samples, taken from different parts of the mine, are also occasionally sent. If, in the latter case, the average composition of the ore is to be ascertained, and not simply that of the several samples, the whole of the samples of the ore are crushed to coarse powder in an iron mortar, and then passed through a rather coarse sieve. It is subsequently mixed uniformly, and a sufficiently large portion of the coarse powder taken out with a spoon and reduced to powder in a steel mortar, passing the whole of it through a fine sieve. After this fine powder has been again mixed most intimately, about 8 to 10 grams of it is taken and triturated, in small portions at a time, in an agate mortar, until it is reduced to an impalpable powder, so that not the slightest gritty particle can be felt when it is rubbed between the fingers. Average samples are generally already sufficiently fine to require only the last operation.

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* Ann. d. Chem. u. Pharm. 61, 249.

As regards the temperature at which the powder is to be dried, if the whole of the moisture is to be expelled without disturbing any of the water of hydration, the temperature employed must be 120° C. (this is the result of the author's own experiments, see Expt. No. 89). In this case it is best to use the drying disc described in § 31 (fig. 42); the finely powdered substance is placed in one of the pans and exposed to the temperature indicated for an hour and a half. But, as there appears to be at present an almost universal understanding in the manganese trade to limit the drying temperature to 100°, the fine powder is exposed in a shallow copper or brass dish, for 6 hours, to the temperature of boiling water, in a water-bath (§ 28, fig. 31). In laboratories where it is often necessary to dry a number of samples at the same time, it is found advantageous to use copper water-baths of the form of rather shallow square boxes, with 4, 6, 12, or more little drying cupboards fixed into the side, separate from each other, so as to be surrounded on all sides, except the front, by boiling water or steam.

When the samples have been dried according to these instructions, they are introduced, while still hot, into glass tubes 12 to 14 mm. long, and 8 to 10 mm. wide, sealed at one end; these tubes are then corked and allowed to cool.

In laboratories where whole series of analyses of different manganese ores are of frequent occurrence, it is advisable to number both the drying dishes and the glass tubes, and always to transfer the samples from the dish to the tube bearing the corresponding number.

II. Estimation of the Peroxide of Manganese in Black Oxide of Manganese.

§ 247.

Of the many methods which have been proposed for the valuation of manganese ores, three are selected as the most expeditious and accurate. The first is more particularly adapted for technical purposes, and is employed almost everywhere for the valuation of black oxide of manganese.

a. Fresenius *and* Will's *Method.*[*]

The principle upon which this method is based has already been applied by Berthier and Thomson.

The following remarks will serve to explain it:—

1. If oxalic acid (or an oxalate) is brought into contact with peroxide of manganese, in presence of water and excess of sulphuric acid, protosulphate of manganese is formed, and carbonic acid evolved, whilst the

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[*] Comp. the papers mentioned in the foot-note † on p. 203.

oxygen, which may be conceived to exist in the peroxide of manganese, in combination with the protoxide, acts on the oxalic acid, and converts it into carbonic acid.

$$MnO_2 + SO_3 + C_2O_3 = MnO,SO_3 + 2CO_2.$$

Each equivalent of available oxygen or, what amounts to the same, each eq. of peroxide of manganese = 43·5, gives 2 eq. of carbonic acid = 44.

2. If this process is performed in a weighed apparatus from which nothing except the evolved carbonic acid can escape, and which, at the same time, permits the complete expulsion of that acid, the diminution in weight of the apparatus will at once show the amount of carbonic acid which has escaped, and consequently, by a very simple calculation, the quantity of peroxide contained in the manganese ore analysed. As 44 parts by weight of carbonic acid correspond with 43·5 of peroxide of manganese, the carbonic acid found need simply be multiplied by 43·5, and the product divided by 44, or the carbonic acid may be multiplied by the factor

$$\frac{43·5}{44} = 0·9887,$$

to find the corresponding amount of peroxide of manganese.

3. Even this calculation may be avoided by simply using in the operation the exact weight of ore which, if it consisted entirely of pure peroxide of manganese, would give 100 parts of carbonic acid. The number of parts of carbonic acid evolved will then give the number of parts of the peroxide contained in 100 parts of the analysed ore. It follows from 2 that the required weight is 98·87.

Suppose the experiment is made with 0·9887 gram of the ore, the number of centigrammes of carbonic acid evolved in the process will express directly the percentage of the peroxide contained in the manganese ore. Now, as the amount of carbonic acid evolved from this weight of peroxide of manganese would be rather small for accurate weighing, it is advisable to take a multiple of this weight, and afterwards to divide the number of centigrammes of carbonic acid evolved by the same number as that by which the unit was multiplied. The multiple which answers the purpose best for superior or high-grade ores is the triple, = 2·966; for inferior ores, it is better to take the quadruple, = 3·955, or the quintuple, = 4·9435.

4. The analytical process is performed in the apparatus illustrated in fig. 99, and which has been described already, Vol. I. p. 337.

The flask *A* should hold, up to the neck, about 120 c.c.; *B* may be somewhat smaller, holding about 100 c.c. The latter is half filled with concentrated sulphuric acid, free from nitric and nitrous acids; the tube *a* is closed at *b* with a little wax ball, or with a very small piece of caoutchouc tubing having a short piece of glass rod inserted in the other end.

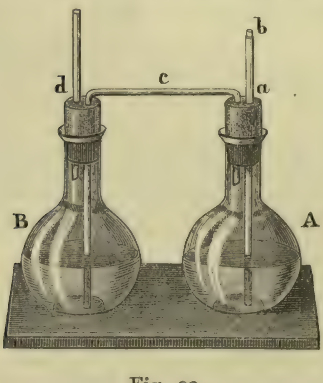

Fig. 99.

A watch-glass, in which weights have been placed equal to 2·966, or 3·955, or 4·9435 grams, according to the quality of the ore (see above) is tared most accurately on a delicate balance; these weights are then removed from the watch-glass, and very cautiously replaced by the black oxide of manganese from the tube, gently shaking out the powder by tapping the tube with the finger, until the equilibrium is exactly restored. The weighed sample is now transferred with the aid of a card, to the flask *A*, 5 to 6 grams of powdered neutral oxalate of soda, or about 7·5 grams of neutral oxalate of potassa in powder, is added, and as much water as will fill the flask to about one-third. The cork is now inserted into *A*, and the apparatus tared on a strong but delicate balance, using first shot, and lastly tinfoil; these must not be placed directly on the scale, but in an appropriate vessel. The tare should be marked and kept under a glass bell jar.

When it has been ascertained that the apparatus is tight (Vol. I. p. 337), some of the sulphuric acid is made to flow from *B* into *A*, by applying suction to *d*, by means of a caoutchouc tube; this rarefies the air in both *B* and *A*, and on again admitting the air, it forces some of the acid from *B* into *A*. The evolution of carbonic acid commences immediately in a steady and uniform manner. When it begins to slacken, more sulphuric acid is made to pass into *A*, and this is repeated until the manganese ore is completely decomposed, which, if the sample has been very finely pulverized, does not require more than five to ten minutes. A too rapid evolution of gas must be avoided, or the sulphuric acid will not remove all the water from the carbonic acid. The complete decomposition of the ore is indicated, on the one hand, by there no longer being any disengagement of carbonic acid, even on allowing a fresh portion of sulphuric acid to flow into *A*; and, on the other hand, by the total disappearance of every trace of black powder from the bottom of *A*.* Lastly, some more of the sulphuric acid is made to pass from *B* into *A*, so as to strongly heat the liquid in the latter, but not higher than 70°, in order to expel the last traces of carbonic acid dissolved. The apparatus must never be exposed to direct sunlight during the analysis, or the ferric oxalate may be decomposed with evolution of carbonic acid (LUCK).† Lastly the wax stopper or india-rubber cap is removed from *b*, and gentle suction applied to *d* until the air drawn out no longer tastes of carbonic acid. The apparatus is allowed to cool completely in the air, then placed on the balance, with the tare on the other scale, and the equilibrium restored. The number of centigram weights added, divided by 3, 4, or 5, according to the multiple of 0·9887 gram used, expresses the percentage of peroxide contained in the ore.

5. As in experiments made with definite quantities of the ore, weighing in an open watch-glass cannot well be avoided, and a slight error may be caused by the dried manganese reabsorbing water from the air, it is better, when very great accuracy is required, to analyse an indeterminate quantity of the ore, and to calculate the percentage as shown above. For this purpose, one of the little corked tubes, filled with the dry pulverized ore, is accurately weighed, and about 3 to 5 grams, according to the quality of the ore, are shaken out into the flask *A*; on reweighing the tube, the exact quantity of ore introduced into the flask is ascertained. To facilitate this operation, it is advisable to scratch on the tube, with a file, marks indicating, approximately, the various quantities

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* If the manganese ore has been pulverized in an iron mortar, however, a few black spots (particles of iron from the mortar) will often remain visible.

† Zeitschr. f. anal. Chem. 10, 322.

which may be required for the analysis, according to the quality of the ore.

6. If the black oxide of manganese is very difficult to decompose, the temperature produced by the mixture of the concentrated sulphuric acid with the water is sometimes not sufficient to effect this completely. In this case, the flask A of the apparatus is placed on an iron plate and the flask B on a board, the iron plate being heated. The temperature, however, ought never to exceed 70°, otherwise the ferric sulphate may cause a decomposition of the oxalic acid (LUCK, *loc. cit.*).

7. If numerous analyses of black oxide of manganese have to be made, it is convenient to suck out the carbonic acid by means of an aspirator. When the air is very moist, any slight error which might be caused by moisture from the air which is sucked through remaining in the apparatus may be obviated, by connecting the end of the tube *b* with a chloride of calcium tube while the air is being sucked through.

With proper care, this method gives most accurate and concordant results, differing, at the most, to the extent of 0·2 per cent. in two analyses of the same ore. The author never found a greater difference than this; if, however, the results of two assays differ by more than 0·2 to 0·3 per cent. at the outside, a third experiment should be made. If the results do not agree as closely as this, the fault lies either in the want of skill on the part of the operator, or of patience in allowing the apparatus to cool, or lastly, in a faulty balance or weights. It is needless to say that care must be taken in powdering and drying the sample, and in ascertaining that the oxalate employed is pure.

8. If the *manganese ores contain carbonates of the alkaline earths*, as is sometimes the case, the process described above will require to be modified, or the results would be incorrect. In order to ascertain whether carbonates of the alkaline earths are present, a sample of the pulverized ore is boiled with water, and nitric acid added; if there is any effervescence, the process is modified as follows (ROHR*):—

After the weighed portion of ore has been introduced into the flask *A*, enough water is added to fill the flask about a quarter full, then a few drops of dilute sulphuric acid (1 part by weight of sulphuric acid to 5 parts water), and the whole warmed with agitation, preferably in a water-bath. After a time a rod is dipped in and the liquid tested to see whether it has a strongly acid reaction; if not, more sulphuric acid is added. As soon as the whole of the carbonates are decomposed by continued heating of the acidified liquid, the excess of acid is completely neutralized with soda solution free from carbonic acid, allowed to cool, the usual quantity of oxalate of soda added, and the process carried out as above.

If no soda solution free from carbonic acid is at hand, the oxalate of soda or oxalic acid (about 3 grams) may be put into a small tube, and the latter suspended in the flask *A* by means of a thread fastened by the cork. When the apparatus is tared and it has been ascertained that it is air-tight, the thread is released and the operation carried out as above.

9. *If the black oxide of manganese contains magnetic iron oxide*† (*or a ferrous compound*), the estimation of the value of the black oxide of manganese, that is the amount of chlorine it is capable of evolving,

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* Zeitschr. f. anal. Chem. 1, 48.

† The presence of the magnetic oxide may be ascertained by its action on an astatic magnetic needle. See MOHR, Zeitschr. f. anal. Chem. 8, 314.

will be inaccurate if the above described methods are employed without modification; the results will be too high, because in carrying out the method the greater portion only and not the whole of the ferrous oxide will be completely oxidised to the ferric state,* moreover on treating the mineral with hydrochloric acid chlorine will not be evolved until the whole of the ferrous iron has been converted into ferric chloride.

The unoxidised portion of the ferrous oxide, and therefore the quantity of ferric oxide which is found in excess by the methods described, is due to the rapidity of the action, and is greater therefore, the more rapidly the operation is conducted.

By a slight modification of the method, however, perfectly satisfactory results may be obtained with black oxide of manganese containing ferrous oxide. Luck† has shown that the ferrous oxide is almost entirely oxidised if some acetate of soda is introduced into the decomposition flask.

If the black oxide of manganese contains ferrous oxide therefore, it suffices, as a rule, to introduce into the decomposition flask about 6 c.c. of a solution of acetate of soda (1 : 9); the operation being otherwise conducted precisely in the ordinary way. It is preferable to effect the decomposition somewhat slowly.

Instead of ascertaining the amount of carbonic acid by the loss of weight of the apparatus, it may be determined as first suggested by Kolbe, by receiving it in a weighted absorption apparatus. This modification of the process is preferred by those analysts who have no large balance capable of weighing very accurately and by those who prefer weighing on one balance rather than two. It is convenient to employ the method described in Vol. I. p. 340, *e*, using a simplified form of apparatus. The carbonic acid evolved passes first through two U-tubes 170 mm. long in the limb and 18 mm. wide, of which the first is empty and the second filled with chloride of calcium (p. 10 this vol.). The carbonic acid at its exit from these tubes passes into two smaller U-tubes 110 to 120 mm. long and 15 mm. wide. These are $\frac{5}{6}$ths filled with coarsely granulated soda-lime, and at the end where the gases pass out, $\frac{1}{6}$th with chloride of calcium; these tubes are weighed before and after the experiment. A small safety tube follows this, and is filled with soda-lime in the lower part and with chloride of calcium in the upper; lastly, there is a small U-shaped tube containing a little water so as to allow of the progress of the operation being observed, and beyond this an aspirator.

The manganese ore is now introduced into the decomposition flask along with the oxalate of soda (if the manganese ore contains magnetic oxide of iron some acetate of soda must be added, see above), and dilute sulphuric acid (1 vol. concentrated acid to 2 of water) allowed to run in through the funnel tube. Care must be taken that the apparatus is not exposed to direct sunlight, and that the temperature of the decomposition flask, which should be heated gently on an iron plate, does not rise above 70°.

If the manganese ore contains carbonates of the alkaline earths, this process affords a convenient means of first ascertaining the amount of carbonic acid in them by adding a slight excess of dilute sulphuric acid, heating gently, and aspirating purified and dry air through the apparatus, and then, after neutralizing the free acid, estimating that evolved from the oxalate of sodium by the action of the manganese ore and sulphuric acid. It is scarcely necessary to mention that for the absorption of larger quantities of carbonic acid, a potash apparatus may be substituted for the soda-lime tube, placing after it a **U**-shaped tube filled half with soda-lime, half with chloride of calcium.

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* Compare Teschemacher and Smith, Zeitschr. f. anal. Chem. 8, 509; Scherer and Rumpf, *Ibid.* 9, 46; Pattinson, *Ibid.* 9, 509; Luck, *Ibid.* 10, 310.

† Zeitschr. f. anal. Chem. 10, 317.

b. BUNSEN'S *Method.**

About 0·4 gram of the black oxide of manganese, reduced to the very finest powder, is weighed off and introduced into the small flask *d*, illustrated in § 130, fig. 85, Vol. I. p. 292, together with some compact pieces of magnesite, and pure fuming hydrochloric acid is poured over it; the process is conducted exactly as in the analysis of chromates. The mixture is boiled until the ore is completely dissolved and all the chlorine expelled, which is effected in a few minutes. Each eq. of iodine separated, and determined as in § 146, corresponds with 1 eq. of chlorine evolved, and accordingly with 1 eq. of peroxide of manganese. In skilful hands, but only in skilful hands, this method gives very good results.

For dissolving the manganese ore and absorbing the evolved chlorine by iodide of potassium solution, the author recommends the apparatus described in Vol. I. p. 361. There should be no delay in estimating the liberated iodine immediately after the completion of the decomposition or the amount will be increased in consequence of the decomposition of the hydriodic acid which is set free, and the result obtained will be too high.

c. *Method, using Iron.*

If the manganese ore is heated with hydrochloric acid and excess of ferrous chloride, the amount of which is known, the chlorine corresponding with the available oxygen of the manganese ore unites with the ferrous chloride and converts it into ferric chloride. As the amount of this can be ascertained by estimating the unaltered ferrous chloride by PENNY'S method (Vol. I. p. 220), the value of the manganese ore expressed as peroxide can easily be calculated. This method, which was given in the 5th edition, has been submitted to critical examination in the author's laboratory by SHERER and RUMPF,† but the results were unsatisfactory, being too low and not sufficiently concordant, owing to small portions of the chlorine escaping without acting on the ferrous chloride.

PATTINSON‡ has obtained good results by a modification of this method, employing sulphuric acid instead of hydrochloric acid. He recommends the following process. About 2 grams of fine iron wire, previously ignited and accurately weighed, are dissolved with the aid of heat in 90 c.c. of pure dilute sulphuric acid (1 part by weight of the concentrated acid to 3 of water) in a 600 c.c. flask, which is arranged as shown in fig. 80 (Vol. I. p. 216), about 2 grams of the finely powdered manganese ore (accurately weighed) are introduced, and the mixture boiled gently until all the ore is dissolved (which with soft specimens takes place very quickly, whilst hard ones require about 15 min.) The water which has come over, together with some more, is allowed to flow back, the whole then diluted to about 250 to 300 c.c., and when cold the excess of ferrous oxide is estimated with dichromate of potassa (Vol. I. p. 220) or with permanganate of potassa (Vol. I. p. 215). The difference gives the quantity of iron which has been converted by the oxygen of the black oxide of manganese from ferrous chloride to ferric chloride.* This difference multiplied by $\frac{43\cdot5}{56}$ or 0·7768, gives the amount of peroxide in the analysed ore.

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* Closely allied to BUNSEN'S method is that of GAY-LUSSAC, extensively employed in France, in which the chlorine evolved is passed into milk of lime, and the chloride of lime solution formed estimated volumetrically (§ 233). SHERER and RUMPF (Zeitschr. f. anal. Chem. 9, 48 and 51), in a critical investigation of this method, obtained results by no means favourable; and in a comparative trial with PERREY'S method (Chem. Centralbl. 1878, 15), the results obtained by GAY-LUSSAC'S process were the lowest.

† Zeitschr. f. anal. Chem. 9, 46.

‡ *Ibid.* 9, 510.

It should be noted that if the black oxide of manganese contains more than 78 per cent. of peroxide, either more iron wire or less of the ore must be taken.

III. Estimation of Moisture in Manganese.

§ 248.

In the purchase and sale of black oxide of manganese, a certain proportion of moisture is usually assumed to be present, and usually a percentage is fixed within which the moisture must be confined. It may be laid down as a rule that in estimating the moisture the same temperature should be employed as that at which the drying for the purpose of determining the peroxide is effected (§ 246, 1).

As the amount of moisture in an ore may be altered by the operations of crushing and pulverizing, the experiment should be made with a larger sample of the coarsely crushed mineral. In taking this it is best to employ a round glass vessel, 80 to 100 mm. in diameter, and 0·3 mm. high, having a flat bottom and closed with a ground glass plate of equal diameter, or a tin box of the same size and form furnished with a well-fitting lid. The vessel is weighed, first empty, and then filled with the manganese ore, and closed. After removing the glass plate or lid, it is placed, without the cover, in a water, oil, or air bath, and heated until the weight is constant. The vessel must be covered before weighing.

If the moisture in a manganese ore is not to be estimated on the spot where the heap is, but in the laboratory, a fair average sample of the ore must be packed in a strong, perfectly dry, and well-corked bottle.

IV. Estimation of the Amount of Hydrochloric Acid required for the complete Decomposition of the Manganese Ore.

§ 249.

Different manganese ores, containing the same amount of available oxygen, or, as it is usually expressed, of peroxide, may require very different quantities of hydrochloric acid to effect their decomposition and dissolve them, so as to give an amount of chlorine corresponding with the available oxygen in them;—thus, an ore consisting of 60 per cent. of peroxide of manganese and 40 per cent. of sand and clay, requires 2 eq. hydrochloric acid to 1 eq. of available oxygen; whereas an equally rich ore containing lower oxides of manganese, ferric oxide, or carbonate of lime will require a much larger proportion of hydrochloric acid.

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* In very precise experiments, the weight of the iron must be multiplied by 0·996, since pianoforte wire as a rule contains only about 99·6 per cent. of iron (Pattinson takes it at 99·9 per cent.).

If the quantity of hydrochloric acid required to decompose the ore is to be determined, the following process is employed:

The strength of 10 c.c. of a moderately strong hydrochloric acid (of sp. gr. about 1·10) is determined by means of an ammoniacal solution of sulphate of copper (§ 216); 10 c.c. of the same acid is then warmed with a weighed quantity (about 1 gram) of the manganese ore, in a small long-necked flask, fitted with a reflux condenser. As soon as the manganese is decomposed, a somewhat stronger heat is applied for a short time, so as to expel the chlorine which still remains in solution; care must be taken, however, to avoid heating longer than is absolutely necessary, as it is of importance to guard against the slightest loss of hydrochloric acid. The flask is allowed to cool, the contents diluted with water, and the free hydrochloric acid remaining is titrated with an ammoniacal solution of sulphate of copper. The difference of the two titrations gives the amount of hydrochloric acid required to effect the decomposition of the manganese ore.

As is well known, in the manufacture of chloride of lime a preparation, "Weldon mud," is made by treating the chloride of manganese with hydrate of lime and air according to the methods proposed by **Weldon**, and this is used again for preparing chlorine. The available oxygen in Weldon mud, usually $CaO,2MnO_2$ is best estimated by **Bunsen**'s method; methods *a* and *c* being less suitable on account of the large amount of chloride of calcuim present. The estimation of the amount of hydrochloric acid required to decompose the Weldon mud is best ascertained by the method given in § 249.

B. Manganese ores in general. Determination of the amount of metallic manganese they contain.

§ 250.

Manganese ores were formerly used almost exclusively in the preparation of chlorine, or as an oxidising agent in glass manufacture; but since its employment for the preparation of manganese iron, the amount of metallic manganese in it has become of great importance.

For estimating this, a great number of new methods have been introduced in addition to those already known; but as these, which are mostly volumetric methods, are connected with the analysis of iron, they will not be considered here, but hereafter in § 255.

In this place, the only method described will be that which has been in use for some years in the author's laboratory. It is, indeed, somewhat more than many would require, but leaves nothing to be desired as regards accuracy, and has the advantage of allowing the other constituents of the ore to be determined.

About 1 gram of the mineral, dried at 100°, is dissolved in hydrochloric acid, the solution evaporated to dryness, the residue warmed with hydrochloric acid, water added, and the solution filtered and diluted to 500 c.c. The residue should be tested as to its freedom from manganese by fusing a portion of it with carbonate of soda with access of air. If manganese is still present, the whole of the residue must be decomposed by fusion with carbonate of soda, the silicic acid separated by hydrochloric acid, and the filtrate added to the original solution.

If the solution is poor in iron, ammonia must be added *until it is feebly alkaline*, and the mixture at once filtered into a flask containing some acetic acid; the precipitate is washed slightly, dissolved in hot hydrochloric acid, allowed to cool, and 10 c.c. of chloride of ammonium solution (not much more than this) added, and the iron then carefully and accurately precipitated as basic salt as described in **82** Vol. I. p. 437.

3a. If, on the other hand, the solution is rich in iron, 20 c.c. of chloride of ammonium should be added, and the iron at once precipitated as basic salt by the method given; the precipitate after being washed slightly, is then again dissolved in hydrochloric acid, 10 c.c. of chloride of ammonium solution added, and the precipitation as basic salt repeated.

After it has been washed, a portion of the basic iron salt is tested for manganese by fusing it with carbonate of soda with free access of air, so as to make certain that the separation is complete.

The filtrate is united with the washings, a little free acetic acid added, the whole concentrated by evaporation to about 300 c.c. and allowed to cool; the solution is then rendered *very slightly* alkaline with ammonia (to separate a trace of alumina) and filtered from the slight precipitate usually produced. After washing somewhat, this precipitate is dissolved in hot hydrochloric acid, again precipitated with ammonia and collected. From the appearance of the precipitate, whether white or brownish, it can easily be seen whether it is necessary to repeat the solution and precipitation. The washings are added to the filtrate, slightly acidified with acetic acid, some acetate of ammonia added, and the whole treated with sulphuretted hydrogen. This usually produces a small black precipitate (sulphide of cobalt, &c.) which is filtered off, the filtrate concentrated as much as necessary, and the manganese estimated as sulphide according to § 109, 2.

The electrolytic estimation of manganese has been worked out by LUCKOW [*] and by A. RICHE.[†] As, however, it is necessary first to remove iron, and then to concentrate the solution to a very small volume (the manganese is deposited as peroxide at the positive pole), and the precipitation must take place from a sulphuric or nitric acid solution, this method presents no especial advantage.

13. NICKEL COMPOUNDS.[‡]

A. Nickel ores, Nickelstein, and other intermediate products of Nickel manufacture.

§ 251.

In the analysis of copper-nickel, antimonial nickel, nickelstibine, and nickel glance, it is necessary as a rule to separate nickel, cobalt, iron, arsenic, antimony and sulphur, and sometimes lead; in white nickel pyrites, copper and bismuth are also present, whilst nickel pyrites generally contains only nickel, cobalt, iron, copper and sulphur in determinable quantities. In the analysis of nickeliferous copper, and iron pyrites also, it is only these elements as a rule, apart from the silicic acid and the alkaline earths, which have to be considered. The kupfer nickelstein obtained as an intermediate product in the preparation of copper-nickel from nickeliferous ores consists principally of copper, iron nickel, cobalt and some sulphur, but arsenic, antimony, and occasionally lead, are often present. The amount of nickel in ores and metallurgical products varies greatly, and since the preparation of nickel has become of such great industrial significance, these are often the subjects of quantitative analysis. As a rule, it is sufficient to estimate the amount of nickel *plus* cobalt present, or of nickel and of cobalt, or of nickel, cobalt, and copper. The following sections, therefore, are confined to the determination of these metals, and sometimes reference is made to the first part of this work for further examination of the precipitates, &c., obtained during the operations.

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[*] Zeitschr. f. anal. Chem. 8, 24. [†] *Ibid.* 17, 216.

[‡] The cobalt compounds are examined in exactly the same way as the nickel

First Method.

A portion of the finely powdered mineral or product from the smelting furnace containing about 0·5 to 1·0 gram of nickel is treated with hydrochloric acid, adding nitric acid from time to time until all that is soluble is dissolved. The solution is repeatedly evaporated almost to dryness with hydrochloric acid to remove excess of nitric acid, and the residue taken up with hydrochloric acid and water, and filtered. If any sulphur remains, the residue must be ignited with access of air, and then treated repeatedly with hydrochloric acid and some nitric acid. If the residue is not quite white, it must be fused with some acid sulphate of potassa, and the melt treated with hydrochloric acid and water, or it may be fused with carbonate of soda, the melt treated with water and hydrochloric acid, and the silicic acid separated, and treated with hydrochloric acid. The solution obtained by one or other of these processes *is added to the original solution.* This is then treated in the following manner:

Sulphuretted hydrogen is passed through the solution, containing hydrochloric acid in sufficient quantity (400 c.c. of the solution should contain about 40 c.c. of hydrochloric acid of sp. gr. 1·12), in order to throw down all the metals capable of being precipitated by this gas. For this purpose the gas should be passed first at about 70°, and then in the cold. The filtrate is heated, and then nitric acid is gradually added so as to convert all the ferrous oxide into ferric oxide. When the solution has cooled a little, excess of ammonia is added, the impure hydrated ferric oxide washed somewhat, dissolved in hydrochloric acid, and the solution largely diluted. To this, 30 c.c. of chloride of ammonium solution is added, and then, in the cold, a dilute solution of carbonate of ammonia until the liquid acquires a turbid appearance, although there is no actual precipitate; if allowed to remain, the solution should not become clear again, but the turbidity should

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compounds, in fact, the three methods which are described in § 251 can be used for either. For testing nickel and cobalt ores in the dry way by Plattner's method (conversion of the nickel and cobalt into arsenides), see Muspratt's Chemistry, third edition.

increase. The liquid at this time has a distinctly acid reaction. It is now heated to boiling, and the precipitate of basic ferric salt washed with boiling water containing some chloride of ammonium, first by decantation, and subsequently on the filter. A portion of the precipitate must be tested for nickel by dissolving it in hydrochloric acid, repeating the precipitation as basic salt, and testing the filtrate with sulphide of ammonium. If nickel is present, the whole of the precipitate must be dissolved in hydrochloric acid, and the ferric oxide again thrown down as basic salt. The two or three filtrates which contain the nickel and cobalt are mixed, acidified with acetic acid, then rendered slightly alkaline with ammonia and concentrated by evaporation. If there is a slight precipitate (hydrated ferric oxide or alumina), it must be collected, dissolved in hydrochloric acid, precipitated with excess of ammonia, and the same operation again repeated. The filtrate or filtrates which contain all the nickel and cobalt are acidified with acetic acid, 30 to 50 c.c. of a solution of acetate of ammonia (1:10) added, and sulphuretted hydrogen passed for some time through the liquid heated to about 70° until it smells strongly of the gas. When the precipitation is complete, the sulphides of nickel and cobalt are collected, washed thoroughly, rinsed into a beaker and the filter incinerated. The filtrate is concentrated by evaporation, hydrosulphide of ammonium added, and then acetic acid, when very often a further small quantity of the sulphides of nickel and cobalt are thrown down. As a matter of precaution, the filtrate is again tested in like manner in order to be certain that all the nickel and cobalt have been converted into sulphides.

The sulphides of nickel and cobalt which have been washed into the beaker, and also the filter ash, are treated with hydrochloric acid, with the addition of nitric acid, until they are completely decomposed and the metals dissolved; the solution is then evaporated with hydrochloric acid to remove nitric acid, diluted with water, filtered, the filter incinerated, and the hydrochoric acid solution of the filter ash added to the filtrate. The solution is now precipitated by potash solution, best in a large platinum dish, pouring the nickel solution into the heated potash which must be in excess. The precipitate thus obtained must be most thoroughly washed with boiling water, first by decantation and then on a filter,* and after partially or completely drying, it is gently heated in a Rose's crucible, first with the cover on and then with access of air. It is now heated more strongly until the filter is completely incinerated, and subsequently for some time in a current of pure hydrogen until the weight is constant. The metallic nickel and cobalt in the crucible are treated with boiling water; if the reaction is alkaline, or the solution contains chlorine or sulphuric acid and leaves a residue when evaporated on platinum foil, the metallic residue must be exhausted with boiling water and again ignited in a current of hydrogen and weighed.

The metals are now dissolved in nitric acid, usually leaving a small residue of silicic acid which should be collected on a small filter and its weight ascertained. The nitric acid solution is nearly neutralised with ammonia, excess of carbonate of ammonia added, the mixture heated gently for a long time and the small precipitate of hydrated ferric oxide and hydrate of alumina collected; it is then dissolved in hydrochloric acid, the solution again precipitated with carbonate of ammonia, and the small precipitate ignited first in the open air and then in a current of hydrogen. Its weight, together with that of the silicic acid, is subtracted from the weight of the metals.

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* The author finds that the statements of Finkener (Handbuch der analyt. Chem. von H. Rose, 6 Aufl. von Finkener. Bd. ii. 136) and Busse (Zeitschr. f. anal. Chem. 17, 60), that hydrated oxide of nickel is somewhat soluble in water is correct, but the trace which dissolves is so minute that it can have no appreciable effect on the result. Compare analyt. Beilage, No. 90.

It is easy to see that in most cases it would be more convenient and quicker to incinerate the small filter with the silicic acid, and that with the alumina and ferric oxide, in the same crucible, and then, after igniting them in a current of hydrogen, to weigh the two impurities together. If, however, the silicic acid or the alumina, &c., appears bluish from the presence of cobalt, the one or the other must be fused with some carbonate of soda and the silicic acid or alumina, &c., separated in the pure state and weighed. As metallic nickel occasionally contains small quantities of manganese, a little phosphate of ammonia must be added to the blue ammoniacal nickel solution obtained when separating the impurities, and the whole allowed to remain for a time in order to see whether any ammonio-phosphate of magnesia separates, which in that case is weighed as pyrophosphate of magnesia and calculated as magnesia. If much cobalt is present, ammonio-phosphate of cobalt is precipitated along with the ammonio-phosphate of magnesia. In that case it is necessary, after washing the precipitate with water containing ammonia, to dissolve it in acetic acid, add acetate of ammonia, and precipitate the cobalt with sulphuretted hydrogen (see p. 301); the filtrate is then concentrated, and on the addition of ammonia and a little phosphate of ammonia, the magnesia salt is thrown down in the pure state.

We must now turn to the sulphuric or hydrochloric acid solution occasionally obtained by the decomposition of that portion of the earthy residue insoluble in nitric and hydrochloric acid, and which contains a small amount of the heavy metals (see above). The most simple method would seem to be to add the solution to the main solution before precipitating with sulphuretted hydrogen. This, however, has the disadvantage of uselessly introducing a relatively large amount of alumina into the solution, which is extremely inconvenient. It is therefore better to treat this small amount of solution separately, first passing sulphuretted hydrogen to remove the metals of the fifth and sixth groups, then, after heating the filtrate with nitric acid, to precipitate with ammonia, wash the precipitate, dissolve it in hydrochloric acid, and again precipitate with ammonia. The small quantity of nickel present is then separated from the united filtrates by sulphuretted hydrogen, as in the case of the principal solution. This small quantity of sulphide of nickel is then dissolved in nitric acid along with the larger quantity (see above).

If the nickel and cobalt have to be determined separately, the separation is effected by means of nitrite of potassium by the methods given in § 160, 9, if there is relatively little cobalt and much nickel; if, however, but little nickel and much cobalt is present, it is better to employ that given in § 160, 10, *b.*, using cyanide of potassium and chlorine or bromine.

The most convenient method is to make the nitric acid solution, obtained by treating the sulphides of nickel or cobalt, up to 250 c.c., and to estimate the nickel and cobalt in 100 c.c. as previously prescribed, whilst in a second 100 c.c., or in the whole remaining 150 c.c., either the cobalt or the nickel is estimated, according to circumstances.

The metals after being weighed must be treated, to remove impurities, precisely in the manner already described for nickel and cobalt. If the cobalt has been precipitated from the hydrochloric acid solution of nitrate of cobalt and potassa by caustic potash,* the filtrate and washings must be treated with sulphide and ammonium. If a slight precipitate of sulphide of cobalt is formed, the cobalt in it is determined as sulphate of cobalt (§111, 2, *b*.) In order to avoid this double estimation of the cobalt, it is far preferable to supersaturate with ammonia the hydrochloric acid solution of the nitrate of cobalt and potassa, precipitate the cobalt as sulphide by means of sulphide of ammonium, dissolve it in nitric acid, evaporate down the solution with sulphuric acid and weigh the sulphate of cobalt (§ 111, 2, *b*).

In case it is not deemed advisable to divide the nickel-cobalt solution, the ammoniacal solution obtained in purifying the weighed nickel and cobalt is acidified with acetic acid, both metals are reprecipitated as sulphides, dissolved in nitric acid, and either the cobalt or the nickel is estimated in the solution by the method described, the metal undetermined in either case being estimated by difference.

When *very little* cobalt is present along with much nickel, all the cobalt may be first thrown down along with some of the nickel, and the separation of the two metals then undertaken. For this purpose both metals are dissolved in hydrochloric acid, the solution neutralised as far as possible with carbonate of soda, and the whole of the cobalt together with part of the nickel precipitated by the careful addition of a weak alkaline solution of hypochlorite of soda to the heated solution. If the operation is conducted so that at least two parts of nickel are present to one of cobalt the precipitate is sure to contain all the cobalt. The colour of the solution of the brownish-black hydrated oxide in hydrochloric acid is an indication as to whether the correct proportion has been attained. If this is nearly colourless or has a greenish or reddish tinge all the cobalt is precipitated, but if it shows a deep red then a further partial precipitation is necessary (FLEITMANN).† The separation is then effected in the hydrochloric acid solution by nitrate of potassa as previously described.

If it is necessary to estimate the copper also in ores or furnace products, the sulphuretted hydrogen precipitate first obtained is treated as in § 261.

Second Method.

According to CLASSEN,‡ nickel, like zinc, can be separated from ferric oxide as oxalate. The author as yet is unable to offer any opinion on this method. The confirmatory analyses mentioned by CLASSEN gave very satisfactory results. In applying this method to nickel ores, &c., a solution is made as in Method 1, and the metals precipitable by sulphuretted hydrogen from acid solution are removed in a similar manner. The sulphuretted hydrogen is then driven off, the ferrous salt oxidised by boiling with nitric acid, and the whole evaporated to complete dryness on the water-bath. The residue is then treated with about seven times its bulk of a solution of neutral oxalate of potassa (1 : 3) warmed for fifteen minutes in the water-bath, and the undissolved ferric oxide brought into solution by the addition of acetic acid drop by drop. If sufficient oxalate of potassa has been added, the solution is clear and of a greenish tinge.

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* For another method of estimating the cobalt in nitrite of cobalt and potassium see BRAUNER, Zeitschr. f. anal. Chem. 16, 195.

† Zeitschr. f. anal. Chem. 14, 76.

‡ *Ibid.* 16, 471; 18, 189; 18, 386.

The solution is heated to boiling, and at least an equal volume of 80 per cent. acetic acid is added, the mixture being stirred meanwhile, whereby the oxalates of nickel and cobalt are thrown down. The oxalate of nickel has a more or less pronounced crystalline appearance only when the quantity of nickel is small. For this reason CLASSEN worked only with quantities of from 0·1 to 0·2 gram. The mixture is now heated for six hours at about 50°, filtered hot, and the precipitate thoroughly washed with a mixture of equal volumes of concentrated acetic acid, alcohol and water. After drying the oxalate of nickel and burning the filter-paper on a platinum wire, the two are heated in a covered platinum crucible, very gently at first, then gradually at a higher temperature, and finally strongly and for a sufficient length of time with free access of air; the protoxide of nickel thus obtained is weighed; insufficient washing of the oxalate of nickel leaves the protoxide of nickel contaminated with carbonate of potassa. This is known if the residue, on being warmed with water, gives an alkaline reaction; in that case, the protoxide of nickel must be thoroughly washed with hot water and weighed again. If it contains cobalt, the incinerated residue, after washing if necessary, is reduced by heating in a current of hydrogen and weighed as metal. For separation of the nickel and cobalt see the first method.

Third Method.

Deposition of Nickel, otherwise of Nickel and Cobalt, by Electrolysis.

The estimation of nickel by electrolytic precipitation, to which W. GIBBS* directed attention in 1864, has had a more extended application in the hands of C. LUCKOW†; the MANSFELD Ober-Berg und Hütten-direction; ‡ HERPIN,§ F. WRIGHTSON,‖ T. SCHWEDER,¶ and W. OHL.** Through their investigation it is known that nickel and cobalt are not precipitated by the electric current from solutions containing free acids, but that they are from ammoniacal solutions or solutions of their cyanogen compounds in cyanide of potassium, as well as from solutions of their neutral sulphates after the addition of acetates, tartrates, or citrates of the alkali (LUCKOW).

H. FRESENIUS and F. BERGMANN†† have recently carefully investigated the conditions which appear to be the most favourable for quantitative estimations in this way. Ammoniacal solutions should be used and must contain a sufficient excess of free ammonia to remain strongly ammoniacal throughout. The presence of sulphate of ammonia or phosphate of soda (M. S. Cheney and E. S. Richards)* facilitates deposition, whilst chloride of ammonium hinders or prevents it; nitrate of ammonia also acts disadvantageously. The following may be regarded as favourable conditions for the deposition of nickel and also of cobalt:

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* Zeitschr. f. anal. Chem. 3, 334.

† Dingler's polyt. Journ. 177, 235.

‡ Zeitschr. f. anal. Chem. 11, 10; 14, 350.

§ *Ibid.* 15, 335.

‖ *Ibid.* 15, 300.

¶ *Ibid.* 16, 344.

** *Ibid.* 18, 523.

†† *Ibid.* 19, 314.

The current from a Clamond pile (compare § 261) is chosen of such a strength as to produce 300 c.c. of oxy-hydrogen gas per hour. The nickel or cobalt should be present, as neutral sulphate, in the proportion of 0·1 to 0·15 gram in 200 c.c. of an aqueous solution containing 2·5 to 4 grams of ammonia and 6 to 9 grams of sulphate of ammonia, both calculated in the dry state. The distance of the lower edge of the tared platinum cone, which forms the negative pole, from the circular foot of the platinum spiral forming the positive pole (see § 261), should be from 3 to 5 mm. The beaker containing the solution is covered by a large watch-glass having suitable openings for admitting the battery wires. In proportion as the nickel is deposited, the colour of the solution diminishes, and directly it becomes quite colourless a few drops of the liquid are tested with sulphocarbonate of potassa, when if a scarcely perceptible rose-red coloration only is observed, the precipitation may be considered as complete. Cobalt solutions at first deepen in colour by the absorption of oxygen, but gradually become lighter and ultimately colourless. In this case the operation is discontinued as soon as the sulphocarbonate test yields a scarcely perceptible wine-yellow coloration.

As soon as the deposition is completed, the liquid is drawn off by means of a water pump or an aspirator into a flask fitted with a two-holed cork, and this is also employed for removing the washings and the final rinsings with the wash-bottle. The wires must not be disconnected until the termination of the washing, when the cone is suspended over a hot iron plate until quite dry, allowed to cool and weighed. The nickel on the platinum cone has a fine glossy appearance, cobalt is less lustrous.

The manner of employing the electrolytic process to nickel ores, nickelstein, &c., depends on the condition and proportion of the other metals present along with the nickel and cobalt. The former can always be removed by Method 1, the sulphides of nickel and cobalt are then dissolved in nitric acid with the addition of hydrochloric acid, and the solution, after digestion with the necessary proportion of sulphuric acid, is supersaturated with ammonia; if necessary more sulphate of ammonia can be added so as to obtain the favourable conditions mentioned above. Sometimes the foreign metals in the ores can also be entirely removed by electrolysis (compare § 264).

B. Commercial metallic Nickel (Nickel cubes and granular Nickel).

§ 252.

Commercial metallic nickel contains about 97 to 98 per cent. of nickel and in addition some cobalt, copper and iron; sometimes traces of arsenic and antimony are present and generally a little lime, magnesia, alumina, and silica; sometimes traces of alkali, and very often small quantities of carbon and sulphur. Frequently the analysis is intended to give the average composition of a parcel, in which case the analyst receives a larger or smaller number of cubes, each taken from a different box. Under these circumstances, as the individual cubes cannot be divided, the only course to pursue is to dissolve the whole in nitric acid after weighing. As a rule, a small insoluble residue is left, which may contain carbon, sulphur, slag and silica. After filtering through a filter which has been dried at 100°, the filtrate and washings are collected in an accurately tared measuring flask, of $\frac{1}{2}$, 1, or 2 litres capacity as required, whilst the washed residue is dried at 100° and weighed. The filtrate and washings are diluted up to the mark, accurately weighed, and well mixed.

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* Zeitschr. f. anal. Chem. 17, 215.

I. Examination of the Solution.

a. So much of it as will contain about 0·5 to 1·0 gram of nickel is measured off into a light tared glass vessel and accurately weighed. Measuring serves merely for estimating approximately the correct quantity, the exact amount being ascertained by weighing, as the total weight of the liquid is known. The solution is evaporated to dryness with hydrochloric acid, the residue heated with hydrochloric acid, the silica separated, and the liquid, now free from nitric acid, and containing about 10 c.c. of hydrochloric acid to each 100 c.c. of water, is treated with sulphuretted hydrogen at 70°. The precipitate is collected on a filter, washed thoroughly, and used for a qualitative examination of the metals contained in it. The filtrate and washings are concentrated by evaporation, and after driving off the sulphuretted hydrogen are boiled with some nitric acid, an excess of ammonia added, and the precipitate collected and washed; this is dissolved in hydrochloric acid, and the ferric oxide then precipitated as a basic salt by nearly neutralizing with carbonate of ammonia and boiling. The filtrate, added to the first ammoniacal main filtrate, is acidified with acetic acid, and precipitated hot by sulphuretted hydrogen; and in this precipitate, along with any blackish precipitate which may possibly be obtained from the filtrate on adding to it ammonia, sulphide of ammonium, and then acetic acid, *the nickel, together with the small quantity of cobalt*, is determined by the first method given in § 251, where all the details are accurately described.

Of course the second or third methods given in § 251 can also be employed for estimating the nickel and the small proportion of cobalt.

b. A larger quantity of the solution, containing say 4 to 5 grams of nickel, is measured and weighed, and *the silica* and metals of the fifth and sixth groups separated as in *a*, the precipitate containing the latter is washed, and *the copper* therein estimated as well as other metals which may be present. The filtrate is treated as under *a*, any *iron and alumina* present being determined in this portion. As, in consequence of the excess of ammonia employed, alumina may be found in the ammonical nickel solution, and as probably some of the alumina is not completely thrown down on the basic precipitation of the ferric oxide, the solutions containing nickel are united, and after being acidified with acetic acid, ammonia is carefully added in very slight excess, and the whole allowed to remain for some time at a gentle heat. If any flakes of alumina separate, they are filtered off and added to the basic precipitate before beginning the separation and estimation of the ferric oxide and alumina. The solution, whether it has remained clear or has been filtered from alumina, is now acidified with acetic acid, warmed, precipitated with sulphuretted hydrogen, and the precipitate collected; the filtrate is treated with ammonia, a little sulphide of ammonium is added, and finally acetic acid until the solution is acid. If in this way a somewhat blackish precipitate is produced, it is collected on a filter after prolonged warming, and added to the main precipitate thrown down by sulphuretted hydrogen from the acetic acid solution. In this precipitate, the cobalt alone, which from the larger quantity taken will generally be found in weighable amount, is estimated. On deducting the cobalt from the nickel + cobalt found in 1, from the amount of nickel is determined.

The filtrate, freed from the last traces of nickel, is now evaporated to dryness in a large platinum dish, the ammoniacal salts are driven off, and the *lime*, *magnesia*, and the *alkalies* (if present) are estimated (§ 154, 6, and § 153, 4, *b*).

c. Lastly, another portion of the solution, containing about 10 grams of nickel, is measured, and after the free nitric acid has been removed as far as possible by evaporation, it is diluted with water, nearly neutralised with ammonia, and the distinctly acid solution treated with chloride of barium, and allowed to remain for some time. If a small precipitate of sulphate of barium is formed it must be determined, as it corresponds with the sulphur which has been converted into sulphuric acid when dissolving the nickel.

II. Examination of the Insoluble Residue.

The residue, dried at 100° and weighed, is ground to a uniform powder, and the sulphur is estimated in an aliquot part of it, by fusing with carbonate and nitrate of potassium (Vol. I. p. 383, 1 *a*). The remainder is fused with carbonate of soda with the addition of a small amount of nitrate of potassa, and the silica, alumina and other compounds present determined in the fused mass, carbon being estimated by difference. If the insoluble residue is very small, it is generally sufficient to allude to it in the report of the analysis as "residue insoluble in nitric acid."

14. Iron Compounds.

A. Iron Ores.

The ores of iron which occur most usually, and consequently those most frequently examined, are hematite, limonite, bog-iron-ore, magnetite, and spathic iron ore. In some cases, a complete analysis is required; in others, simply the estimation of certain constituents (the iron, phosphoric acid, sulphuric acid, &c.); in others again, merely the determination of the iron.

I. METHODS FOR COMPLETE ANALYSIS.

§ 253.

a. Hematite.

If the mineral contains only ferric oxide, moisture, and gangue insoluble in acids, the first method should be employed for their analysis; but if it contains also phosphoric acid, alkaline earthy carbonates, protoxide of manganese, &c., the second method is preferable.

First Method.

The ore is reduced to an impalpable powder and dried at 100°.

a. A portion is weighed off in a platinum or porcelain boat,* and this is inserted in a porcelain tube, a stream of dry air being passed through the tube, and the substance heated until all the water is expelled; it is then allowed to cool in the current of air, and weighed. The loss of weight corresponds with the *water*.

b. The boat is re-inserted in the porcelain tube and heated by means of a gas or charcoal furnace (this vol. pp. 12, 13, 14) (for several hours) in a stream of pure dry hydrogen, until no more water is formed, raising the temperature at the end as high as possible; it is allowed to cool in the hydrogen and weighed. The loss of weight corresponds with the *oxygen* combined with the iron to form ferric oxide, and from it the amount of the latter can be calculated.

c. The loop of the boat containing the reduced iron is fixed to the end of a platinum wire, and the boat is placed in a $\frac{1}{4}$-litre flask, some water added, then dilute sulphuric acid, and the flask is closed, but not air-tight, the platinum wire being fixed by the cork. The finely divided iron dissolves with evolution of hydrogen, the action being assisted by a gentle heat. As soon as this is completed, the boat is raised, rinsed, and the liquid heated to gentle ebullition, to expel hydrogen, allowed to cool, filled up to the mark, shaken, allowed to settle, 100 c.c. of the liquid taken out, and the *iron* determined by means of permanganate or dichromate of potassa (Vol. I. p. 215 or 220). The result must correspond with that obtained in *b.* If they should not agree satisfactorily, the cause may lie in the solution of ferrous oxide having become slightly oxidized. In this case, another 100 c.c. is boiled with a little zinc (preferably in a stream of carbonic acid), and then the titration with permanganate is repeated.

d. The *residue* which has settled to the bottom of the flask is collected on a filter, washed, dried, ignited, and weighed; it usually consists of silicic acid, but may contain also alumina and titanic acid. It is fused with acid sulphate of potassa and dissolved in cold water, the *silicic acid* remains undissolved, and the *titanic acid* is separated by long boiling (§ 107). After passing sulphuretted hydrogen, if any iron is present, the *alumina*, or the alumina along with any ferric oxide that may be present, can be precipitated from the filtrate by ammonia; these can be separated as described in § 160, A. 2.

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* Glass tubes, even when of very refractory glass, are not to be recommended, as on long continued heating the boat is often melted to the glass.

Second Method.

This is similar to the process employed for limonite, see *b*.

The decomposition and solution of the hematite will not take more than a few hours, if the mineral is very finely powdered and is digested at an elevated temperature below the boiling point with a sufficiency of fuming hydrochloric acid. The separated silicic acid is to be tested for titanic acid as described on p. 263 of this vol. If any is present, some of it must have passed into solution; if the quantity appears to be weighable, it is better to estimate the titanic acid in a separate portion of the hematite sample.

b. Brown Iron Ore (Limonite).

Limonite sometimes contains small quantities of ferrous oxide along with hydrated ferric oxide, besides oxides of manganese and alumina, sometimes small quantities of the oxides of copper, zinc, nickel, and cobalt, and often also some lime and magnesia, silicic acid (in combination with bases), carbonic acid, phosphoric acid, and sulphuric acid, and more or less quartz-sand or gangue insoluble in hydrochloric acid. Sometimes limonite also contains organic substances.*

1. The analysis is begun by finely pulverizing the ore, and drying the powder under the desiccator or at 100°, according to circumstances. The powder prepared in this way is introduced into a dry glass tube and tightly closed; the quantity must be sufficient for the entire analysis.

2. To determine the *water*, it usually suffices to heat a portion to redness in a platinum crucible, the water being estimated from the loss of weight. If, however, the ironstone contains carbonates of the alkaline earths, ferrous oxide, or weighable quantities of organic matter, this method is not available, and the water must then be determined by direct weighing (compare § 36 and § 235 I. *e*).

3. About 10 grams of the powdered ore is weighed out, gently ignited in a platinum basin in such a manner as to be certain of destroying all the organic matter present, and digested in a flask with fuming hydrochloric acid at a moderate heat until completely decomposed. A little chlorate of potassa is added, and after heating for some time the mixture is transferred to a porcelain dish, 5 to 10 grams of pure chloride of sodium is added, and the whole evaporated to dryness on the water-bath,† the residue is then moistened with hydrochloric acid, gently heated, diluted with water, filtered into a 500 c.c. flask, and washed; the undissolved residue is dried, ignited, and weighed, the solution being filled up to the mark and weighed.

4. The residue consists of quartz-sand or gangue, and separated *silicic acid*. It may be isolated and determined by boiling an aliquot

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* Besides the above, which are generally found in limonite, traces of other substances are often also detected by a very thorough analysis. Thus A. Müller (Ann. d. Chem. u. Pharm. 86, 127) found in a bean-ore, smelted at Carlshütte, near Alfeld, weighable traces of potassa, arsenic acid, and vanadic acid, and unweighable traces of chromium, copper, and molybdenum. Titanic acid also is sometimes found. For an iron ore very rich in vanadium, comp. H. Deville (Compt. rend. 49, 210; Journ. f. prakt. Chem. 84, 255).

† If a weighable quantity of arsenic is present, the hydrochloric acid solution must not be evaporated. In that case, also, the addition of chloride of sodium is of course unnecessary.

part with a solution of carbonate of soda (§ 237, 2. *b*). If it is desirable to ascertain more precisely the nature of the *gangue*, which often still contains some iron, the residue insoluble in carbonate of soda is carefully washed and treated as described for the analysis of silicates (§ 140 II. *b*), or another aliquot part of the original residue insoluble in hydrochloric acid is so treated. If the residue has a reddish appearance, a further examination is absolutely necessary.

5. 250 c.c. of the solution from 3 is largely diluted (to about 1 litre), 25 c.c. of chloride of ammonium solution added, the mixture nearly neutralised with ammonia, a dilute solution of carbonate of ammonia added until the liquid remains slightly turbid, and the whole boiled, thus precipitating the ferric oxide and a portion of the alumina (compare § 160, 3, and this vol. p. 299). If the iron solution is not colourless after boiling, a few c.c. of a neutral solution of acetate of ammonia is added and the liquid heated repeatedly to boiling; any phosphoric acid, &c., present comes down with the ferric oxide (see 6). The liquid is decanted hot, filtered, and washed with hot water containing a little chloride of ammonium. The precipitate is in the meantime kept moist. If the brown iron-ore is rich in manganese, it is necessary to repeat the precipitation of the iron as basic salt (compare this vol. p. 299).

6. A little acetic acid is added to the filtrate or filtrates from 5, to which the washings have been united, and the whole concentrated by evaporation, and left to cool; ammonia is then added until just alkaline and the precipitated alumina filtered off, the filtrate being collected in a flask containing a little acetic acid. After a brief washing, the precipitate is dissolved in hydrochloric acid, again thrown down by ammonia in the same way, filtered into the first filtrate, washed, and this precipitate together with that obtained in 5, is treated as in 7. These precipitates contain the ferric oxide, the alumina, and silicic acid which were dissolved, and also the phosphoric acid (and arsenic acid). The solution filtered from the hydrate of alumina and containing a slight excess of acetic acid, is concentrated by evaporation if necessary.

7. The precipitates mentioned in 6 are dissolved in hot hydrochloric acid and the solution made up to 250 c.c.; if any silicic acid remains undissolved it is collected on a filter and weighed.

a. 50 c.c. of the solution is precipitated by ammonia (Vol. I. p. 192 *a*); the weight of the precipitate expresses the sum of the following substances present in the solution, namely, ferric oxide and alumina, silicic acid, and phosphoric acid (also arsenic acid). The *silicic acid* is separated by prolonged digestion with fuming hydrochloric acid, and finally by fusion with acid sulphate of potassa, and weighed.

b. 50 c.c. are employed for the determination of the *ferric oxide* by stannous chloride (Vol. I. p. 225). If a gravimetric analysis is preferred, the method given in Vol. I. p. 435, 2 is recommended.

c. If, from the weighed precipitate obtained in 7 *a*, the silicic acid, ferric oxide and phosphoric acid determined in 10 (also the arsenic acid if present) are deducted, this gives the weight of the *alumina*.

8. To the solution from 6, containing free acetic acid, ammonia is added until it is slightly alkaline, then acetic acid again until distinctly acid, and lastly some acetate of ammonia; sulphuretted hydrogen is now passed in, the solution being gently heated. If a slight usually black precipitate is formed, it is filtered off, and the *manganese* thrown down from the filtrate as sulphide, and estimated as such

(§ 109, 2). The first precipitate is dissolved in a little brominated hydrochloric acid, and after heating to drive off the free bromine, any copper present is precipitated by sulphuretted hydrogen, and any *nickel*, *cobalt*, and *zinc* present is determined in the filtrate according to § 160, 6, *b*.

9. The liquid separated from the sulphide of manganese is acidified with hydrochloric acid, evaporated, the ammonia salts driven off, and the *lime* and *magnesia* determined in the residue (§ 154, 6).

10. The remaining 250 c.c. of the solution from 3 is employed for the determination of the *phosphoric acid* or *phosphoric* and *arsenic acids*, and also the *copper*. If phosphoric acid alone is to be estimated, and it is not present in too small a quantity, the solution is evaporated to dryness on the water-bath with repeated additions of nitric acid, and the residue taken up by nitric acid and precipitated by molybdenum solution, the phosphoric acid being determined according to § 134 *b*, β. If, on the other hand, there is also enough copper or arsenic acid present to be estimated, or if the quantity of phosphoric acid is very small, the solution is treated repeatedly with sulphuretted hydrogen at 70°, filtered, and the copper, the arsenic, or both (§ 164), estimated in the precipitate, and the phosphoric acid in the solution, according to § 135 *h*, γ (Vol. I. p. 317). The phosphoric acid which separates along with a small quantity of ferric oxide is then determined according to § 134 *b*, β.

11. To determine the amount of *sulphuric acid* if any is present, 3 to 5 grams of the dried powdered ore is fused with 1 part by weight of carbonate of soda and 1 part by weight of nitrate of potassa (F. MUCK*) in a platinum crucible over a Berzelius spirit-lamp; the fused mass is treated with boiling water, filtered, and the sulphuric acid estimated in the filtrate (Vol. I. p. 383, 1 *a*).

12. If the ore contains *ferrous oxide*, a suitable quantity is digested with strong hydrochloric acid (containing no free chlorine) in a 250 c.c. measuring flask until completely decomposed, preferably in a current of carbonic acid. It is filled up to the mark, mixed, and the ferrous chloride determined in an aliquot part according to § 112, 2, *b*. If the brown iron ore can be decomposed by prolonged heating with dilute sulphuric acid this method is preferable; the ferrous oxide is then estimated according to § 112, 2, *a*. When manganese is present as peroxide, it must not be forgotten, in calculating the ferrous oxide, that the oxygen liberated from the manganese oxide when dissolving has converted a corresponding amount of the ferrous iron into the higher oxide. By deducting the ferric oxide corresponding with the amount of ferrous oxide from the quantity obtained in 7, the amount of ferric oxide in the mineral is ascertained.

13. If *carbonic acid* is present it is best determined as described in Vol. I. p. 340.

14. In testing for *titanic acid* the best way is to heat a separate portion of the mineral to redness in a current of hydrogen until the ferric oxide is completely reduced, and then to treat the residue as described in this volume (p. 308 *d*).

15. If the brown iron ore contains *vanadium* and *chromium*, like the oolitic iron-ore from Haverloh in the Harz, the finely powdered ore is mixed with one-third its weight of nitrate of potassa and exposed to a

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* Zeitschr. f. anal. Chem. 7, 416.

low red heat for about an hour; the mass is then powdered and extracted with not too large a quantity of water. To the solution, which is yellow if chromium is present, dilute nitric acid is added with the greatest care, stirring continually, until it is only slightly alkaline. The solution must never be allowed to become acid or the nitrous acid liberated would reduce the chromic and vanadic acids. The precipitate formed (silicic acid and hydrate of alumina) is filtered off, and the filtrate is precipitated by chloride of barium with the addition of ammonia; the precipitated chromate and vanadate of barium is collected on a filter, washed thoroughly, and boiled with dilute sulphuric acid in not too great excess. The reddish-yellow solution filtered from the sulphate of barium is saturated with ammonia, strongly concentrated by evaporation, and a piece of chloride of ammonium put into the liquid. In proportion as the latter becomes saturated with this salt, vanadate of ammonia separates as a white or yellow crystalline powder; when the separation is complete, it is collected, washed with a saturated solution of chloride of ammonium, dried and heated gradually with full access of air. In this way the vanadium is obtained as the dark red, almost black, vanadic acid, which is a red liquid when strongly heated, and solidifies to a crystalline mass on cooling (F. WÖHLER*). On adding sulphurous acid to the filtrate from the vanadate of ammonia, the chromium is precipitated as the hydrated oxide. For another method of detecting traces of chromium in iron ores see A. TERREIL.†

c. Bog Iron Ore.

The bog iron ores, which consist essentially of sedimentary hydrated ferric oxide resulting from the oxidation—mostly assisted by organic action—of compounds of ferric oxide dissolved in the water, are characterised by the invariable presence of phosphoric acid, occasionally as much as 4 per cent., and also by the presence of humic acids. They, moreover, always contain silicic acid (in combination and as quartz-sand), sometimes sulphuric and arsenic acids, oxide of manganese is always present, and ferrous oxide, alumina, lime and magnesia frequently.

After the ore has been reduced to powder and dried, a portion of it is heated in an inclined platinum crucible, at first gently to burn off the organic acids, the temperature being then gradually raised and maintained for some time at a bright red heat. The loss corresponds with the amount of water and organic substances.

Another portion is treated by the method given in *b* for limonite (this vol. p. 309), after the sample has been very gently ignited so as to destroy the organic substances.

If the organic acids are to be detected and determined, a larger portion of the finely pulverized ore is boiled with pure solution of potassa, until it is converted into a flocculent mass. It is then filtered and the filtrate treated as directed § 209, 10 to 12.

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* Die Mineralanalyse in Beispielen, second edition, p. 150.

† Zeitschr. f. anal. Chem. 4, 440.

d. Magnetic Iron-Ore.

The magnetic iron ores contain the iron as ferroso-ferric or magnetic oxide. In analysing them, the possible presence of titanic acid, magnesia, and gangue must be ascertained; in the earthy ores of this class, a high percentage of protoxide of manganese is found, and sometimes small amounts of oxide of copper. Phosphoric acid occurs but rarely in magnetic ironstone, and then only in small proportion.

The ore is analysed in the same way as hematite, and afterwards, in a separate weighed portion which has been dissolved in hydrochloric acid in a current of carbonic acid, the ferrous oxide is determined volumetrically by means of dichromate of potassa (Vol. I. p. 220, *b*), or the ferric oxide by means of stannous chloride (Vol. I. p. 225).

c. Spathic Iron Ore.

Spathic iron ore contains ferrous carbonate, associated usually with manganous carbonate and carbonate of the alkaline earths, and is often mixed also with clay and gangue. Sometimes also part of the ferrous carbonate has been converted into hydrated ferric oxide.

The powdered mineral is dried either in the air or at 100°.

a. The water is determined as in § 36.

b. The carbonic acid is best determined as in Vol. I. p. 340.

c. A third portion, from 8 to 10 grams, is dissolved in hydrochloric acid, some chlorate of potassa is added to convert all the ferrous chloride into ferric chloride, and the liquid after being boiled until it ceases to smell of chlorine, is treated as directed for brown iron ore in *b*.

d. In a fourth portion of the powder, dissolved in hydrochloric acid in a current of carbonic acid, either the ferric oxide is estimated volumetrically by stannous chloride (Vol. I. p. 225), or the ferrous oxide with dichromate of potassa (Vol. I. p. 220).

II. ESTIMATION OF THE IRON IN IRON ORES.

§ 254.

1. Volumetric Methods.

Many volumetric methods have been proposed with the above object and adopted, and some of them have again fallen into disuse. The permanganate of potassa method, long considered as the easiest and best, sustained a blow by the discovery of LÖWENTHAL and LENSSEN that correct results could be obtained in hydrochloric acid solutions only when the conditions of testing, the amount of hydrochloric acid present, the degree of dilution, and the temperature, were identical (see Vol. I. p. 219).

Of the methods here described, the first is especially recommended on account of its simplicity and accuracy.

First Method.

Five grams of the ore *as finely powdered as possible*, either air dried or dried at 100°, are gently ignited until all the organic matter present is destroyed, and then heated in a flask with hydrochloric acid at a temperature which is below the boiling point. For red ironstone, fuming hydrochloric acid is absolutely necessary, and it is also advisable to use it for brown iron ore. When the decomposition and solution are, as far as possible, complete, chlorate of potassa is added *if the ore contains ferrous oxide*, the mixture is heated for a considerable time, transferred to a porcelain dish, rinsed in and evaporated almost to dryness on a water-bath. It is then certain that the chlorate of potassa is completely decomposed and all the free chlorine driven off. Hydrochloric acid is added to the residue, then water, the liquid is filtered into a 500 c.c. measuring flask, and the residue thoroughly washed.

If the ironstone contains no ferrous oxide, the contents of the flask are diluted with water, filtered into a 500 c.c. measuring flask and the residue washed. In either case, the flask is filled up to the mark, the contents mixed, and as a precaution a small portion of the liquid is tested with ferricyanide of potassium to be sure that no ferrous chloride is present. The iron is then determined twice volumetrically by means of stannous chloride (Vol. I. p. 225), usually 100 c.c. of the solution each time.

For preserving the solution of stannous chloride, the apparatus shown in fig. 100 can be used instead of that described in Vol. I. p. 226, particularly if the solution is only required for use at comparatively long intervals, as in this apparatus it can be kept for some time without undergoing change. The stannous chloride solution is run off from the bottle *a*, by means of a syphon *e*. The air which enters is first made to pass through the U-tubes *b* and *c*, and the bottle *d*, all of which contain pumice moistened with a strongly alkaline solution of pyro-

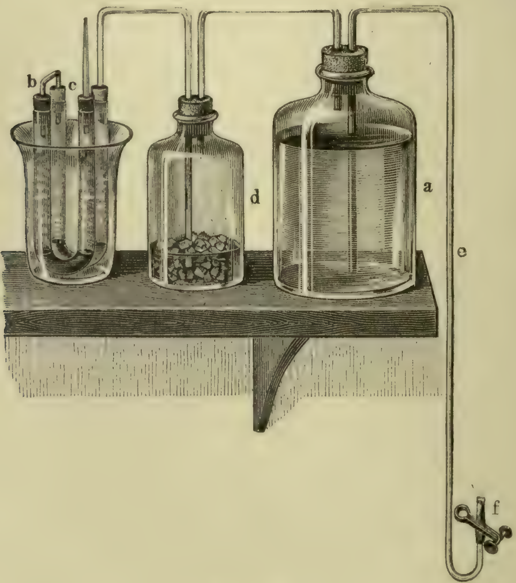

FIG. 100.

gallate of potassa. This solution is prepared in the tubes and bottle by pouring in at the same time concentrated potash-lye and pyrogallic acid solution some time before the apparatus is required. As the oxygen of the air is rapidly absorbed by the pyrogallate of potassa, in a short time the vessels contain nothing but pure nitrogen. When everything is ready, a glass tube is affixed to the india-rubber tubing *f*, the syphon is filled by suction, and the pinchcock closed. To fill a pipette or pinchcock burette, the point of it is placed in the india-rubber tube after the pinchcock of the burette has been pushed back over the delivery tube, the pinchcock *f* is opened and the liquid allowed to ascend. The pinchcock on *f* is closed first, and then that on the burette, which can now be removed.

The iron contained in the hydrochloric acid solution of the iron ore is ascertained in the prescribed manner. Sometimes small quantities of iron are contained in the residue insoluble in hydrochloric acid; this is notably the case when the residue, either before or after heating to redness, is red or has a reddish appearance. To estimate any iron present in the residue, it is decomposed by fusing it with carbonate of soda, separating the silicic acid (Vol. I. p. 348, *b*), and determining the iron in the hydrochloric acid solution by stannous chloride; if, however, this solution is added to the main bulk before making up to the mark, a special titration is avoided.

Second Method.

As far as regards the preparation of a hydrochloric acid solution of the iron ore, containing the iron as chloride, but neither nitric acid nor free chlorine, the process is the same as in the first method, the estimation being made, however, in aliquot parts of the solution, by means of iodide of potassium, in the manner described in Vol. I. p. 227 β.

If the residue insoluble in hydrochloric acid still contains any iron compound, it is treated as in the first method, and the ferric chloride contained in the solution is also estimated by means of iodide of potassium. In the author's experience, the first method yields more trustworthy results than the second in the analysis of ironstone, the latter being better adopted for estimating smaller quantities of iron.

Third Method.

A hydrochloric acid solution is prepared as in the first method, diluted, reduced with zinc* in a current of carbonic anhydride (Vol. I p. 224, 3*a*), and the ferric chloride is determined by Penny's method (Vol. I. p. 220), or by means of a titrated solution of permanganate of potassa, observing the special precautions recommended in Vol. I. p. 219 γ, for solutions containing ferrous oxide and hydrochloric acid. If the insoluble residue still contains iron, it must be decomposed as in the first method.

Fourth Method.

About 0·5 gram of the very finely powdered iron ore is fused with

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* Zinc pounded in a mortar, heated to 210°, and sifted so as to obtain a uniform rather coarse-grained powder, is far better suited for this purpose than granulated zinc or powdered sheet-zinc (T. M. Brown, Zeitschr. f. anal. Chem. 18, 98).

3 to 4 grams of acid sulphate of potassa or acid sulphate of soda, using a gentle heat at first, which is gradually increased, and keeping it fused for a long time, but not long enough for the second equivalent of sulphuric acid to be entirely volatilized; the residue is then dissolved in dilute sulphuric acid, the solution reduced by boiling with zinc* in a current of carbonic acid (Vol. I. p. 224, 3*a*), and the ferrous oxide finally determined by means of a standard solution of permanganate of potassa as in Vol. I. p. 215, 2*a*. The difficulty in carrying out this process consists in the fact that the decolorization of the solution is no criterion of the completion of the reduction; hence when it seems to be finished, a drop of the solution must be taken out and mixed on a porcelain plate with sulphocyanide of potassium solution. If there is a distinct reddening, the reduction is not yet completed. The reaction of sulphocyanide of potassium with ferric oxide is so delicate, that no notice need be taken of very weak colorations. Naturally the results are correct only when a complete decomposition and dissolution of the ferric oxide has been effected.

2. Gravimetric Methods.

Of these, FUCHS's method is to be preferred,† the unfavourable statements made in respect of it by certain chemists having been refuted by J. LÖWE ‡ and R. KÖNIG § in 1857. It is to be noted, however, that this method is almost entirely supplanted by the volumetric methods.

a. The ordinary method (as described by LÖWE, *loc. cit.*

If the ore intended for analysis is of a superior kind, 1 to 1·5 gram is taken, if inferior, 2 to 3 grams; this is reduced to a very fine powder, and heated with strong hydrochloric acid in an obliquely placed long-necked flask of about 500 c.c. capacity; when all the ferric oxide is dissolved, small pieces of fused chlorate of potassa are gradually added, until the liquid smells distinctly of chlorine, and the heating is continued until the odour of chlorine is no longer perceptible. The liquid is then diluted with water until the flask is half full, and a sound cork is inserted, in which a glass tube, open at both ends, about 10 inches long, and not too narrow, is fitted air-tight; the flask is placed in a slanting position, and heated for, *at least*, 15 minutes to moderate boiling, in order to insure the expulsion from the water and from the flask of every trace of chlorine and atmospheric air.

While keeping the solution in *continuous ebullition*, the cork is taken out, and a strip of pure clean sheet copper, attached to a thin platinum wire, is lowered slowly into the liquid, inserting the cork again so as to keep the wire in position; in doing this, the copper strip must be allowed at first to hang in the neck of the flask until it has become sufficiently hot to allow of its immersion in the fluid, without danger of spirting. The cork is then loosened again, and the strip of copper let down horizontally to the bottom of the flask, so that it is completely covered by the liquid; the cork is now firmly screwed in, the flask placed once more in a slanting position, taking care during this manipulation to keep the iron solution in *continuous*, though slow and moderate ebullition. The boiling must be continued until the iron in the solution is completely reduced, and it is, therefore, either *quite* colourless, or at all events is so very slightly greenish that it is difficult to distinguish the colour. As a rule, the reduction is completed in about 2 hours, but the boiling may be continued for 3 or 4 hours without the least effect on the accuracy of the results. During the boiling, the strip of copper must always remain completely covered by the liquid; for this reason, it is necessary that sufficient water should be added at first, as any subsequent addition is of course quite impracticable.

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* See footnote, p. 315.

† Journ. f. prakt. Chem. 17, 160.

‡ *Ibid.* 72, 28.

§ *Ibid.* 72, 36.

The strip of copper should weigh about 6 grams; it should be made of copper precipitated by galvanic action, and of the proper breadth and length to pass readily through the neck of the flask and lie at the bottom in a horizontal position. It is scoured clean with sand-paper, weighed, and then attached to the platinum wire.

When the reduction of the ferric chloride is completed, the flask is uncorked, the strip of copper quickly withdrawn from the still boiling liquid by means of the platinum wire, and immersed in a beaker filled with distilled water, taken out again, rinsed by means of the washing-bottle, dried completely between blotting-paper, taken off the platinum wire, weighed, and for each eq. of copper dissolved, according to the equation $Fe_2Cl_3 + 2Cu = 2FeCl + Cu_2Cl$, 1 eq. of iron is reckoned. The copper is found to have lost its original lustre during the operation, and looks dull, but not blackish, as is generally the case if ordinary sheet copper is used. In four analyses of chemically pure ferric oxide, J. Löwe obtained by this process, severally, 99·7, 99·6, 99·6, 99·6 per cent. of ferric oxide.

König's process (*loc. cit.*) is nearly the same. He recommends, however, to keep the strip of copper, after its removal from the boiling liquid, for some time in hot water, so that every portion of the solution which may have penetrated into the pores of the metal may be washed out; then to remove the water by immersion in absolute alcohol, and to remove the latter again by immersion in ether. He also recommends the winding of platinum wire round the strip, which, besides accelerating the reduction, will prevent the loss of small particles of the copper, that might otherwise be caused by the bumping of the metal against the sides of the vessel during the process of ebullition. The results which König obtained by this process, in a series of experiments, varied between 99·5 and 100·5 per cent.

The effect of the slight solubility of copper in boiling dilute hydrochloric acid on the accuracy of the results is within the limits of experimental error (J. Löwe).*

b. *Modified Process.*

If the iron ore contains an appreciable proportion of titanic acid, the process *a* requires, according to Fuchs, certain modifications, for which the original paper on the subject must be consulted,† as cases of the kind are of comparatively rare occurrence.

If the ore contains arsenic acid, the process is inapplicable, as a coating of blackish scales of arsenide of copper would form on the copper. The arsenic acid may be removed, however, by fusing the pulverized ore with carbonate of soda, and extracting the fused mass with water; the residue is dissolved in hydrochloric acid, and the solution treated as in *a*.

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* Zeitschr. f. anal. Chem. 4, 361.

† Journ. f. prakt. Chem. 18, 495; see also König, Journ. f. prakt. Chem. 72, 38.

B. Analysis of different kinds of Iron.

I. CAST IRON.

§ 255.

Cast iron, one of the most important products of metallurgic industry, contains a whole series of elements either mixed in greater or less proportion with the iron, or combined with it. Although the effect which the various foreign substances mixed with the iron have on the quality of cast iron is not yet accurately known, still the fact that they do exercise considerable influence on it is beyond doubt. The analysis of cast iron is one of the more difficult problems of analytical chemistry. The following are the substances to which attention must be directed in the analysis:

Iron, *carbon combined with the iron*, and in the form of *graphite*, nitrogen, *silicon*, *phosphorus*, *sulphur*, potassium, sodium, lithium, calcium, magnesium, aluminium, chromium, titanium, zinc, *manganese*, cobalt, nickel, vanadium, *copper*, tin, arsenic, antimony and tungsten. As a general rule, the elements in italics alone are quantitatively determined.

1. Estimation of the Carbon.

a. Estimation of the total amount of Carbon.

Of the various methods proposed in former times and more recently for the determination of the total amount of carbon in cast iron, those only invariably yield accurate results, in which the carbon is converted into carbonic acid, and weighed as such; on the other hand, all those methods must be considered as less trustworthy, in which the carbonaceous residue left after subjecting the substance to some process of solution, is weighed, the incombustible part thereof determined, and the carbon estimated by difference. The reason why methods of the latter kind cannot be relied on, is simply because the combustible portion of the residues in question is not usually pure carbon. Hence the methods here given are almost all of the former description, being distinguished from one another partly in that the burning of the carbon is performed, either on a residue obtained by dissolving the iron in a suitable manner, or on the mechanically divided iron, or again that the oxidation of the carbon is effected in the wet or dry way; under *α* the methods for obtaining from cast iron a residue containing all the carbon is described, under *β* the determination of the carbon therein, and under *γ* the estimation of the carbon by directly burning the iron.

a. Methods of obtaining a Residue containing all the Carbon of the Cast Iron.

aa. BERZELIUS' *Method** *and its Modifications.*

As in dissolving cast iron in hydrochloric or sulphuric acid the combined carbon is disengaged in the form of hydrocarbons, **BERZELIUS** employed neutral metallic salts to dissolve the iron, especially a solution of chloride of copper† free from excess of hydrochloric acid, or sulphate of copper and chloride of sodium in equal equivalents dissolved in water. He recommends that the solvent be allowed to act in the cold until the colour of the liquid shows that almost all the copper is thrown down, when the solution of copper chloride is renewed or crystallised copper chloride is added. If no more copper is precipitated, either in the cold or on gently warming, the liquid is allowed to stand for another twenty-four hours to make sure. Hydrochloric acid is now added, and if necessary more copper chloride, until the precipitated copper is dissolved; the carbonaceous residue is now collected in a filtering tube containing spongy platinum, and washed, first with water, then with hydrochloric acid, and finally again with water.

This method has, in course of time, become modified, especially has it been found very advantageous to use the double chloride of copper and ammonia instead of chloride of copper (PEARSE‡) (CREATH§) as the dissolution of the iron is greatly hastened; also asbestos‖ filters are now generally used for collecting the carbon.

The solution of the double chloride of copper and ammonium is prepared by dissolving 340 grams of crystallized chloride of copper, and 214 grams of chloride of ammonium in 1850 c.c. of water.

The cast iron should be in a finely divided state, in the form of turnings, borings, or very small pieces. Any oil from the tool used in boring, &c., which may adhere to the iron must be first removed by treatment with ether, and if there is any organic matter mixed with it the iron must be separated by the aid of a magnet. From 2 to 5 grams of the purified, finely divided iron, is taken, and the solution of the double chloride of copper and ammonium is poured on to it in the proportion of 20 to 25 c.c. of the solution to each gram of iron. When all the iron is dissolved, the residue is treated by one of the following methods according as to whether carbon is to be estimated by means of chromic acid or by combustion.

aa. The separated carbon, together with the metallic copper, is collected in an ordinary funnel loosely packed with asbestos, preferably with the aid of the pump, and washed to remove the precipitated cuprous chloride, first with concentrated hydrochloric acid, and then with water or alcohol,* until every trace of hydrochloric acid is removed. If any chlorine compound is left in the residue, this gives rise to chlorochromic acid when it is treated with chromic and sulphuric acids, and the results come out too high. The contents of the funnel, when alcohol is used for washing, must be dried completely.

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* BERZELIUS' Lehrbuch der Chemie, WÖHLER's translation, 10, 118.

† According to H. HAHN (Zeitschr. f. anal. Chem. 4, 210), hydrogen containing hydrocarbons is evolved on dissolving iron in chloride of copper, as a result of the galvanic action set up by the contact of the iron with the precipitated copper, thus causing a loss of carbon. According to MAX BUCHNER, however (*Ibid.* 4, 211), the amount of gas thus disengaged is so small, when the copper chloride employed is quite free from acid, that the loss of carbon is unweighable.

‡ Eng. and Min. Journ. New York, 21, 151; also Zeitschr. f. anal. Chem. 16, 504.

§ *Ibid.* New York, 23, 168; also *ibid.* 16, 504.

‖ The asbestos filter can be conveniently prepared by placing glass wool in an ordinary funnel, pouring on asbestos made into a pulp with water, and washing until no more asbestos fibres are carried through. In this way a good filtering layer of asbestos will be formed on the glass wool (compare SAUER, Zeitschr. f. anal. Chem. 14, 312). The asbestos used must have been exposed to a red heat in a current of moist air to free it from fluorine (compare KRAUT, Zeitschr. f. anal. Chem. 3, 34).

ββ. Hydrochloric acid, and, if necessary, more of the double chloride of copper and ammonium solution, is added to the contents of the vessel until all the metallic copper is dissolved; the carbon is then collected on an asbestos filter,† and washed first with some hydrochloric acid, and subsequently with water or alcohol, until every trace of the hydrochloric acid is removed, after which the contents of the funnel are completely dried at about 100° to 110°.

bb. C. ULLGREN'S *Method.*‡

ULLGREN, instead of using chloride of copper or chloride of copper and ammonium, treats the finely divided iron with a solution of 1 part of sulphate of copper in 5 parts of water at a gentle heat, and ELLIOT § uses the same method. The solvent is easy to prepare, but acts far more slowly than the double chloride of copper and ammonium. To dissolve the precipitated copper, the residue, when this method is used, must also be heated with chloride of copper and hydrochloric acid.

cc. BOUSSINGAULT'S *Method.*‖

The finely divided cast iron is ground up for about half an hour in an agate or glass mortar with 15 times its weight of mercuric chloride, and sufficient water to make a thin paste. After adding more water the whole is transferred to a glass beaker and heated for half an hour at 80° to 100°. It is collected on an asbestos filter, the residue washed thoroughly with hot water, completely dried in an air bath, and gradually heated to redness in a platinum boat in a current of dry hydrogen gas, so as to volatilize the mercurous chloride which is mixed with the carbon. To completely free the hydrogen from oxygen, it is first passed through a long layer of spongy platinum and then through sulphuric acid. For the subsequent treatment, see *β.* (Third method).

dd. W. WEYL'S *Method.*¶

This excellent process possesses the great advantage that it is not necessary to pulverize the iron, as during this operation, as is well known, it is very apt to be rendered impure. Dissolution is effected with the aid of a *weak* galvanic current, using a BUNSEN'S element, the piece of iron to be analysed being made the positive electrode and immersed in dilute hydrochloric acid. The iron dissolves as ferrous chloride without the evolution of any gas from its surface, leaving the carbon behind, whilst the hydrogen escapes from the opposite negative electrode. With a *strong* current, the object would not be effected, for under its influence the iron would readily become passive; under these circumstances chlorine would be evolved from its surface, which would have an oxidizing action on the carbon already separated, and would also form a combination directly with it, which would be decomposed by the current in a manner analogous to hydrochloric acid, carbon being separated at the negative pole as well as hydrogen. It is obvious, that loss of carbon is incurred in both cases, namely, in the first case in the form of carbonic oxide or carbonic acid, and in the second as carburetted hydrogen, which may be formed from the carbon and hydrogen simultaneously separated at the negative pole.

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* L. KLEIN (Zeitschr. f. anal. Chem. 18, 76) gives the preference to alcohol as more easily washing the carbon from the edge of the funnel, and being easier to remove by drying.

† See footnote, ‖ p. 319.

‡ Ann. d. Chem. u. Pharm. 124, 59; Zeitschr. f. anal. Chem. 2, 430.

§ Journ. of the Chem. Soc. 7, 182.

‖ Compt. rend. 66, 873; Zeitschr. f. anal. Chem. 8, 506.

¶ Pogg. Annal. 114, 507; Zeitschr. f. anal. Chem. 1, 112, and 250.

A piece of iron weighing from 10 to 15 grams is chosen and suspended in dilute hydrochloric acid by means of a pair of pincers with platinum points, care being taken that the points of contact of the pincers with the iron are not moistened by the acid, otherwise the carbon separated between the platinum points and the iron would soon very much impede the process of solution. The pincers are connected with the wire of the positive pole, and the platinum foil fixed on the wire of the negative pole is likewise immersed in the acid, the strength of the current being regulated by increasing the distance between the electrodes, so that no ferric chloride is formed, but only ferrous chloride. The formation of the former is immediately rendered evident by the yellowish colour of the streams of concentrated iron solution which descend from the piece of iron. The iron alters but little in outward appearance during the process of dissolution, as the carbon retains the original form of the piece of iron. As soon as the immersed portion of the lump has dissolved (this takes about 12 hours), the operation is interrupted, and the undissolved compact piece of iron is separated from the adhering carbon, dried, and weighed; the loss indicates the amount of substance taken. The carbon is collected on an asbestos filter.

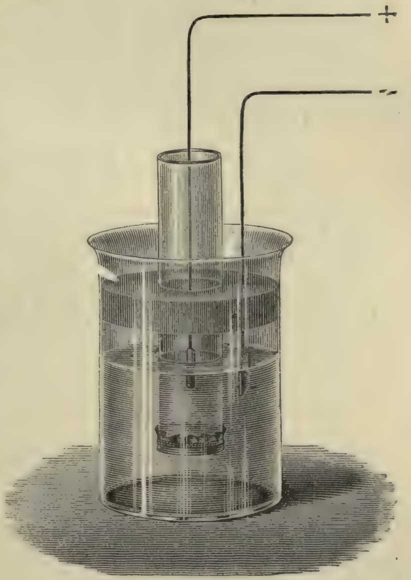

FIG. 101.

If this process is applied to those kinds of iron which deposit carbon in a finely divided state and not in a coherent mass, as "Spiegeleisen" does, the platinum foil of the negative electrode becomes black from the carbon deposited there. RINMANN* first made this observation in treating Bessemer steel by WEYL's method. According to WEYL,† with these kinds of iron the method requires a slight modification, the apparatus shown in fig. 101 being employed. This consists of a glass beaker half filled with dilute hydrochloric acid, containing a glass cylinder (held in place by a suitable disc), closed at the bottom by a bladder or parchment paper, and filled up to the height of the surrounding liquid with dilute hydrochloric acid.

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* Zeitschr. f. anal. Chem. 3, 336.

† *Ibid.* 4, 157.

The cylinder contains the positive electrode, that is the piece of iron, the platinum foil serving as negative electrode being in the space between the cylinder and the beaker. In other particulars, the process is the same as in the preceding method. In this apparatus also, the platinum foil is blackened after several hours' use, but the deposit dissolves in hydrochloric acid, and is iron, not carbon.

ee. WÖHLER'S *Method.*[*]

WÖHLER'S method depends on the fact that when cast iron is heated in a current of chlorine, the whole of the iron volatilizes as chloride, leaving all the carbon behind. It is comparatively rapid and yields very good results, so that many chemists prefer this to all other methods.[†] The iron (1 to 2 grams) is weighed into a porcelain boat, which is inserted into a tube of refractory glass, where it is exposed to the action of chlorine at a low red heat, the gas being dried by passing it over pumice moistened with concentrated sulphuric acid. The treatment is continued until no more ferric chloride is formed, all the carbon remaining in the boat. Care must be taken in drying the chlorine, as if even small quantities of moisture are present, a loss in carbon may occur from the formation of hydrocarbons.

ff. Other Methods.

In addition to the methods *aa* to *ee*, several others have been proposed, notably that in which bromine is employed,[‡] and WEYL'S[§] process, in which dilute chromic acid is used. Some of these are not greatly to be recommended, whilst others have been less carefully investigated than those already described, and on that account any detailed description of them is omitted.

β. Estimation of the Carbon in the residue from a.

The estimation of carbon in the residue obtained in *a* is, as a rule, effected by converting it into carbonic acid and weighing the latter. The most usual processes are by combustion in a current of oxygen (First Method), or by oxidation with chromic acid (Second Method). BOUSSINGAULT estimates the carbon from the loss of weight on combustion (Third Method).

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[*] Zeitschr. f. anal. Chem. 8, 401.

[†] Compare MAX BUCHNER, Berg- und Hüttenmänn, Zeitung. Jahrg. 24, p. 84; Zeitschr. f. anal. Chem. 4, 211; B. KERL, *ibid.*; E. G. TOSH, Chem. News, 1867, No. 401, p. 67, and No. 403, p. 94; Zeitschr. f. anal. Chem. 7, 498, and 8, 401.

[‡] Compare WERTHER, Journ. f. prakt. Chem. 91, 250; Zeitschr. f. anal. Chem. 4, 211.

[§] Zeitschr. f. anal. Chem. 4, 158.

aa. First Method (Combustion of the Carbon and Weighing the Carbonic Acid).

If a residue containing all the carbon, and free from copper, has been obtained in *cc* or *ee*, this will be already in a boat; if, on the other hand, the residue has been collected in an asbestos filter, as in *aa*, *ββ*, *dd*, or as in *bb*, it is transferred, asbestos and all, to a porcelain or platinum boat, all traces of carbon being removed from the funnel by the aid of a wisp of moist asbestos which is also placed in the tray, the contents of the latter being thoroughly dried, if necessary. The boat is then inserted into a tube (this vol. p. 27), the hinder part of which is empty, the fore part being filled with granular copper oxide, and the process carried out exactly as described in this vol. pp. 25–28. The absorption apparatus is best arranged as follows: A tube is fitted directly on to the end *b* of the combustion tube, as shown in figs. 13, 14, or 15, on p. 10 of this volume; this tube contains calcium chloride in both limbs, but the bend between them is filled with lead peroxide enclosed between cotton-wool plugs. As thus prepared, the tube is capable of arresting not only the water but also any sulphurous acid which may be evolved during combustion, as is the case if the residue contains metallic sulphides. Before using, dry carbonic acid is first passed through the tube, and then a continuous current of dry air until every trace of free carbonic acid is removed. The outlet end *g* of the tube is connected with two weighed **U**-tubes (this vol. p. 35) filled with soda-lime and some calcium chloride, the second **U**-tube being joined to a similar but unweighed safety tube (the nearer limb of which contains calcium chloride and the farther limb soda-lime) terminating in a glass tube bent at right angles and dipping into water to the depth of a few centimetres, so that the progress of the operation can be conveniently watched. With regard to the heating, it should be noted that the carbon which has been chemically combined with the iron burns easily, whereas to burn the graphite it is necessary to heat it in a current of oxygen more strongly and for a longer time. As, however, complete combustion is not always obtained in this way, the residue in the boat must be more carefully examined to ascertain that it is quite free from graphite. All things considered, therefore, oxidation by chromic acid is preferable for residues which are rich in graphite.

If the combustion method is employed for residues containing carbon and copper resulting from the dissolution of the iron by sulphate of copper, the residue yielded by 1 gram of iron should be mixed with 50 grams of copper oxide, and the combustion effected as described in this vol. p. 28 *b*. This method, however, cannot be recommended for residues containing graphite, because it is impossible to ascertain whether the graphite has been completely burnt. For a modified process of a gas volumetric estimation of carbon in this way see Parry (Zeitschr. f. anal. Chem., vol. xii. p. 225).

bb. Second Method (Oxidation with Chromic Acid).

The wet process for transforming carbon into carbonic acid by oxidation with dichromate of potassa and sulphuric acid, recommended by the brothers Rogers, and later by Brunner,* was first adopted by

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* Pogg. Ann. 95, 379; Jahresb. von Liebig und Kopp, 1855, 773.

Ullgren, for the estimation of the carbon in carbonaceous iron residues, but in a modified form, chromic acid being substituted for the dichromate of potassa. It ensures complete oxidation of the carbon even in residues rich in graphite, and is particularly useful for the residues from grey pig-iron. The method recommended by Ullgren is first described,* especially on account of its suitability—first, the process of solution is given (compare this vol. p. 320), and then the modification of it.

About 2 grams of the cast iron in the form of borings, if grey, or of coarse powder, if white, is treated in a small beaker at a gentle heat and with stirring, with a solution of 10 grams of sulphate of copper in 50 c.c. water. As soon as the iron is dissolved, it is allowed to settle, and the *clear* solution is decanted, pouring what remains both liquid and solid into the flask *a*, fig. 102; the particles that remain in the beaker are rinsed into the flask with a jet from the wash-bottle, using the smallest possible quantity of water, so that the liquid may not exceed 25 c.c. 40 c.c. of concentrated sulphuric acid, or proportionally more if it was necessary to use more wash-water, is now poured into the flask. When the mixture is cold, 8 grams of chromic

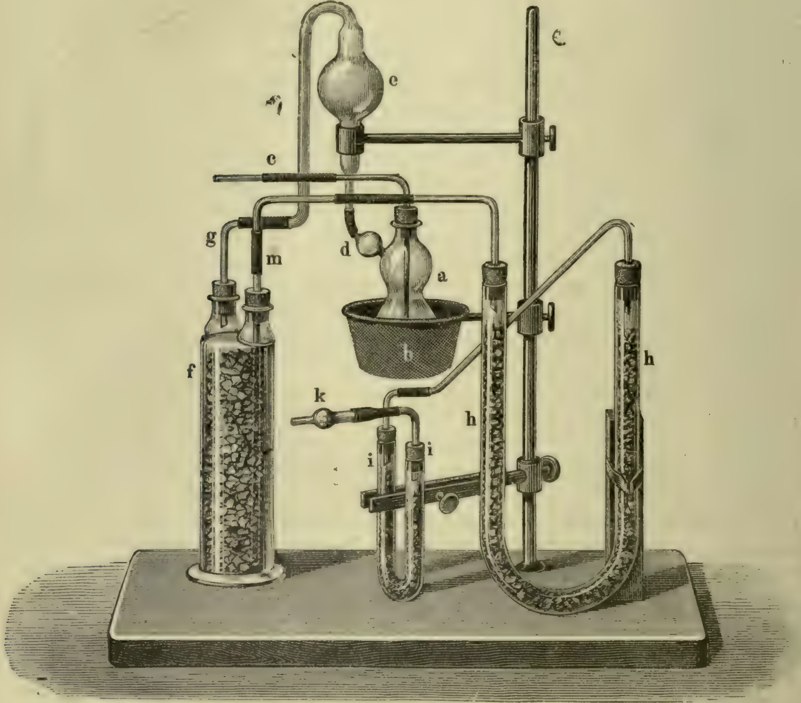

Fig. 102.

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* Ann. d. Chem. u. Pharm. 124, 59; Zeitschr. f. anal. Chem. 2, 430.

acid is added,* and the flask connected with the apparatus for absorbing the carbonic acid. The quantity of carbonic acid resulting from the oxidation of the carbon by the chromic acid corresponds with the total amount of the carbon. The apparatus is represented by fig. 102. The flask *a* which holds 150 c.c., stands in the wire basket *b*; during the operation, *c* is closed with a glass rod, which, when air is drawn through at the end of the operation, is replaced by a potash tube; *e* is connected with the bulb tube *d*, which is fused to the side of the flask; this bulb, which must be of 70 or 80 c.c. capacity, serves to condense the greater portion of the aqueous vapour. The cylinder *f* holds ¼-litre and contains pumice which has been moistened with sulphuric acid, and then heated until the hydrochloric and hydrofluoric acids arising from the chlorides and fluorides contained in this silicate have been entirely expelled. The tube *g* leading into the cylinder terminates just underneath the stopper, whilst the exit tube *m*, on the contrary, reaches nearly to the bottom. *h* contains chloride of calcium, and is 0·6 metre long; *ii* is the weighed absorption tube, filled principally with potash pumice,† but containing a little chloride of calcium at the end. It is connected during the operation with a small guard-tube *k* containing potash.

When everything is ready, the flask is heated gradually until the evolution of gas becomes so violent that the mass threatens to boil over. The temperature is now kept at this same point, as long as the gas is freely evolved, but as soon as it begins to slacken, the temperature is again raised until white vapours begin to ascend into the bulb tube *e*; and, regulating the temperature by this means, the action is carried on until the evolution of gas is only very feeble. *k* is now connected with an aspirator, and the stopcock opened a little before connecting *c* with a potash-tube; *c* should be previously pressed down into *a*, so that it may dip into the liquid. The stopcock of the aspirator is then opened a little more, so that the air bubbles may pass through the liquid in *a* at the rate of about two a second. When 5 or 6 litres of water have flowed out of the aspirator, the whole of the carbonic acid in the apparatus will have been absorbed by *i*. When cold, the latter is weighed, but to make quite sure it is again connected with the apparatus, more air is drawn through it, and it is re-weighed to see whether the weight has increased.

Instead of introducing into the flask *a*, the residue consisting of carbon and precipitated copper obtained by Ullgren's method of solution, the residues obtained by any of the other processes in *a*, or *aa* to *ee*, can be treated in the same way. For those free from copper, somewhat less chromic acid can be used, namely, about 3 grams to each gram of iron. As the decomposing liquid, a mixture of 2 parts of pure concentrated sulphuric acid with 1 part of water is recommended; forms of apparatus other than that described by ULLGREN, may of course be used. CLASSEN * recommends the apparatus he devised for the estimation of carbonic acid, and with which KLEIN † also obtained very good results. This apparatus is shown in fig. 103.

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* The brothers Rogers, and subsequently Brunner, recommended a mixture of dichromate of potassa with excess of concentrated sulphuric acid, but Ullgren prefers chromic acid, as by its use the formation of anhydrous chrome alum is avoided. When concentrated sulphuric acid is employed, this salt is deposited, as a green muddy kind of powder, almost insoluble in water, acids, and alkalies, and tends both to delay and conceal the completion of the oxidation.

† The potash-pumice is prepared as follows: 1 part of caustic potash is dissolved in 3 to 4 parts of water, the solution heated in an iron vessel, and maintained at a temperature somewhat over 100°, while enough granulated pumice stone is stirred in to form a nearly dry mass. It is then put, while still hot, into a bottle with a ground stopper and shaken until the temperature is so reduced that the grains no longer adhere to one another. This preparation absorbs carbonic acid very rapidly and completely; Ullgren says more rapidly than soda-lime.

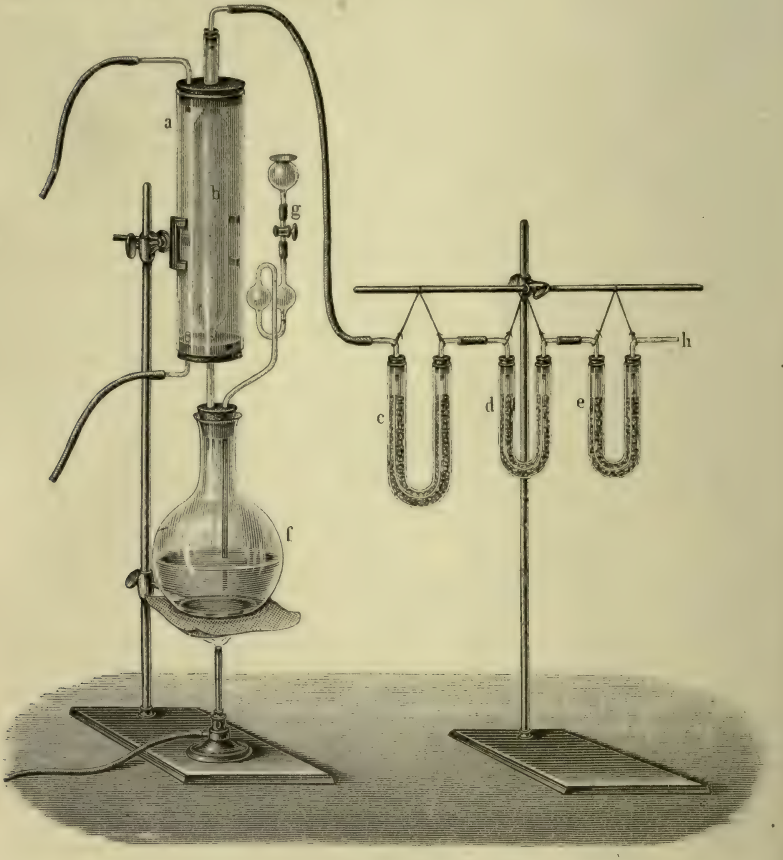

FIG. 103.

Its chief peculiarity is the condenser, which is well adapted for its purpose. It consists of a tube *b*, 27 to 30 mm. wide, with a tube of 15 mm. fused on to its upper extremity, and one of 6 to 7 mm. wide on to its lower end. This tube is inserted in a somewhat wider glass cylinder (the chimney of an Argand burner 230 mm. long and 45 mm. in diameter, will do) through which a current of cold water passes. This condenser so effectually cools the vapours ascending from the 200 c.c.

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* Zeitschr. f. anal. Chem. 15, 288.

† *Ibid.* 18, 76.

boiling flask *f*, that the **U**-tube *c* is sufficient to dry the carbonic acid. This tube contains glass beads on to which enough concentrated sulphuric acid is poured to form a seal in the bend, thus allowing the progress of the operation to be observed :—*d* and *e* are the soda-lime tubes for weighing (this vol. p. 35). The sulphuric acid in *c* need only be renewed after a series of experiments. After the residue containing the carbon, the necessary quantity of chromic acid, and about 50 c.c. of the above-mentioned mixture of sulphuric acid and water are introduced into the flask *f*, *g* is connected with a soda-lime tube, and *h* with an aspirator, and a regular current of air is slowly drawn through the apparatus to prevent the stopping up of the funnel tube. Heat is then applied and very gradually increased, the contents of the flask being finally boiled for about a quarter of an hour; the tubes *d* and *e* are weighed when they are again quite cold.

Instead of CLASSEN's apparatus, that shown on p. 234 of this vol., can be used with the best results, the tubes *i* and *k* being of course omitted. This is so far better constructed than either ULLGREN's or CLASSEN's apparatus, that the air entering and leaving the soda-lime tubes is dried by calcium chloride, whilst in the others, the air entering the apparatus is dried by sulphuric acid, but on leaving it is only dried by calcium chloride.

cc. Third Method. Estimation of Carbon by loss in Weight on Combustion.

BOUSSINGAULT employed this method for estimating the carbon in the residues produced as in *a. cc* (this vol. p. 320). The boat, freed from mercurous chloride and cooled in a current of hydrogen, is weighed, the carbon burnt off, and the residue again weighed after cooling in a current of hydrogen; the loss in weight is reckoned as carbon. If the carbon is from white pig-iron (or from bar iron or steel), it is black, voluminous, easily ignited and burns like tinder, but if from grey iron it contains graphite as well, and requires prolonged heating in a current of oxygen; moreover, the residue must be carefully examined to see that it is quite free from graphite. The fact that the combustible matter in the residue is not absolutely pure carbon but contains hydrogen as well, causes the amount of carbon estimated in this way to be rather too high. According to BOUSSINGAULT's* experiments, however, the error is but small.

γ. REGNAULT's *Method of determining the Carbon by direct Combustion of the Iron.*

In order to directly burn the carbon in cast iron, it must be reduced to the finest powder. The harder kinds are broken on the anvil, stamped in a steel mortar (Vol. I. p. 38, fig. 25), and passed through a plate sieve with very small holes; the softer kinds are filed with a very good, well-hardened file. Samples of iron which cannot be reduced to a very fine powder by these means, are not suitable for treatment by this method.

REGNAULT, who was the first to employ this method of direct combustion, and Bromeis,* both used a mixture of chromate of lead with chlorate of potassa for the process of combustion. Kudernatsch,† who observed that the use of these agents is attended with a slight evolution of chlorine, preferred pure oxide of copper. H. Rose recommended heating to redness with oxide of copper in a current of oxygen gas (this vol. p. 28, *b*); Wöhler used the method described at p. 25, *a* of this vol. (combustion of the cast iron in a boat, in a current of oxygen); Mayer recommended the use of chromate of lead mixed with dichromate of potassa (§ 176). Although no determination of the water is made, it is always advisable to place a chloride of calcium tube between the combustion tube and the potash apparatus, so as to absorb any moisture that may be present.

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* Zeitschr. f. anal. Chem. 10, 114.

These methods, however, are but little used, and give results which are too low, see Tosh‡ and Parry.§

b. Estimation of the Graphite.

α. Another portion of the cast iron is treated with moderately concentrated hydrochloric acid, at a gentle heat, until no more gas is evolved; the solution is filtered through asbestos which has been ignited in a stream of moist air, and the undissolved residue is washed, first with boiling water, then with solution of potassa, after this with alcohol, and lastly with ether (Max Buchner‖); it is then dried, and the graphite converted into carbonic acid, preferably by oxidation with chromic acid (this vol. p. 323). Direct weighing is not recommended, as the graphite is generally impure.

β. In order to estimate the graphite as well as the chemically combined carbon, Boussingault¶ proposed heating the residue (this vol. p. 320), obtained on treating the iron with mercuric chloride, in the air to a temperature a little below dull red heat; in this way the chemically combined carbon is burnt off, leaving the graphite unchanged; the latter is then burnt in a current of oxygen. As Boussingault determined the combined carbon and the graphite by difference, the residue of silicic acid must be heated in pure hydrogen after each combustion in order to bring any iron present into the same condition as it was in the weighed carbonaceous mixture. As finely divided graphite is not altogether incombustible when gently ignited in the air, its estimation by this method may easily come out somewhat too low and that of the combined carbon somewhat too high.

c. Estimation of the Carbon in Combination.

α. The amount of combined carbon is ascertained by deducting the graphite obtained in *b*, *α*, from the total estimated carbon in *a*.

β. Boussingault's method for determining the combined carbon is given in *b*, *β*.

γ. If the kind of iron contains so little chemically combined carbon that estimation by difference (*α*) does not give sufficiently accurate results, the chemically combined carbon must be directly determined. The author's process* for this purpose consists in dissolving the iron in dilute sulphuric acid by warming, passing the mixture of hydrogen and hydrocarbons with air over red-hot oxide of copper, collecting the carbonic acid, after drying, in a soda-lime tube, and calculating the carbon from the increase in weight of the latter.

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* Ann. d. Chem. u. Pharm. 43, 242.

† Journ. f. prakt. Chem. 40, 499.

‡ Zeitschr. f. anal. Chem. 7, 498.

§ *Ibid.* 12, 225.

‖ Journ. f. prakt. Chem. 72, 364.

¶ Ann. chim. Phys. [iv.] 19, 78; 20, 243; Zeitschr. f. anal. Chem. 10, 112.

The iron to be dissolved (1 to 1·5 gram) is placed in the flask *a* of the apparatus figured on p. 234 of this vol. The tube proceeding from the condenser *b* is connected by means of a piece of india-rubber tubing with a descending glass tube bent at right angles in such a way that the ground ends of the glass tubes fit closely to one another. The horizontal portion of the descending tube is then connected by a cork or india-rubber stopper with the hinder part of a combustion-tube. The tube is about 300 mm. long, resting in a furnace, and, in that part (about 150 mm. in length) next the generating flask, is filled, without leaving any visible empty spaces, with asbestos which has previously been heated to redness first in damp and then in dry air; then follows coarse-grained oxide of copper, and lastly a short plug of asbestos. The end of the combustion-tube farthest from the generating flask is connected with a sufficiently large chloride of calcium tube, and this with a smaller light U-tube, accurately weighed and filled with granular soda-lime, and part of the further limb with chloride of calcium. To this is attached a safety U-tube, the limb nearest the soda-lime tube being filled with chloride of calcium, whilst the other contains soda-lime; the whole terminates in an aspirator. After heating the combustion-tube to redness in a current of air free from carbonic acid, and making sure that the apparatus is tight and that on heating the combustion-tube to redness in a current of air free from carbonic acid there is no increase in the weight of the soda-lime tube, *v* (fig. 97, p. 234 of this vol.), which was connected by the rubber tubing above *s*, is replaced by the small funnel-tube, and by a suitable exhaust, by means of the aspirator, enough dilute sulphuric acid (1 part of HO,SO_3 to 5 parts of water) for solution, which must be gradually poured into the funnel-tube, is drawn into the generating flask *a*. The funnel-tube is then again replaced by *v*, and by opening the pinchcock *s*, and the tap of the aspirator, to the requisite extent, a slow current of air is drawn through the apparatus during the whole course of the experiment. The part of the combustion-tube containing the copper oxide is in the meantime kept at a moderate red heat and remains so during the whole operation. The generating flask is now heated on a hot iron plate, to facilitate solution. The operation proceeds quietly, and is at an end in 1½ to 2 hours; towards the last, the contents of the flask are heated to boiling. In the case of iron poor in graphite, it is advantageous to add a very small quantity of spongy platinum, so as to facilitate solution. When hydrogen is no longer evolved, the end of the combustion-tube containing the asbestos is also heated in order to burn off any traces of condensed hydrocarbons; finally, it is allowed to cool gradually in a slow current of air, the increase in weight of the soda-lime tube is determined, and from this the amount of carbon, evolved in the form of hydrocarbons, is calculated.

Naturally this operation can only serve for the estimation of the chemically combined carbon, if it is certain that this carbon is completely volatilized in the form of hydrocarbons. This is the case with numerous kinds of pig-iron, but with many sorts, some hydrocarbons remain behind with the graphite.* Whether this is the case can be easily ascertained by observing if the residue left in the generating flask, after being thoroughly washed with boiling water, gives up carbon compounds to caustic potash, alcohol, or ether; that is, whether these solvents become coloured, and if the alcohol and ether employed, the lye having previously been displaced by water, yield an organic residue on evaporation or not.

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* Zeitschr. f. anal. Chem. 4, 73.

δ. Very often, for practical purposes, an exact determination of the chemically combined carbon is not attempted, a colorimetric estimation being made instead. This method, originated by EGGERTZ,† depends on the fact that the crude iron dissolves in nitric acid, yielding a solution which is of a deeper brown, the larger the amount of combined carbon present. With reference to this method compare also GRUNER,‡ BRITTON,§ HERMANN,‖ CREATH,¶ and MORRELL.**

2. Estimation of Sulphur.

a. Method for Converting the greater part of the Sulphur into Sulphuretted Hydrogen.

This method, devised by the author and first described by LIPPERT,†† subsequently improved by the author,‡‡ and finally simplified by his assistant, Mr. J. MOFFATT JOHNSTON, is best carried out with the help of the apparatus shown in fig. 104.

a is a boiling flask holding about 300 to 400 c.c. in which the iron is dissolved; *b* is a smaller flask, which contains the pure hydrochloric acid used for dissolution; *c* leads to a small, upwardly inclined glass condenser, the tube of which should not be too narrow. The exit tube of this is connected with a U-shaped bulb tube, and this again with an ordinary U-tube (see fig. 95, Vol. I. p. 361), terminating in an india-rubber tube and glass tube in direct communication with the open air or dipping into a flask containing caustic soda. The tubing *d* is connected with a hydrogen apparatus. The hydrogen is purified by being passed first through a potash solution, then through one of permanganate of potassa, and finally through a solution of oxide of lead in caustic potash. The bend of the U-tubes is filled with a solution of bromine in hydrochloric acid.

After about 10 grams of the pulverized iron has been introduced into *a*, and some water added, hydrogen is passed through the apparatus until the latter is filled with it, and the greased tube *e*, which up to the present did not dip into the liquid in *b*, is pushed downward through the caoutchouc stopper until it reaches the hydrochloric acid. The pressure of the hydrogen now forces a portion of the hydrochloric acid into *a*, and the iron begins to dissolve. The pinchcock *f* is now closed and the action of the acid on the iron is assisted by gently heating. Directly the evolution of gas slackens, a fresh portion of acid is forced from *b* into *a* in the manner described above. When dissolution is finished, *e* is drawn up a little way through the stopper, and hydrogen is passed through the almost boiling hot liquid in *a*, so as to drive off all sulphuretted hydrogen from the vessel. If care has been taken that the bromine is present in sufficient quantity, no sulphur separates in the U-tube, and the oxidation of the sulphur is complete. When the operation is ended, the hydrochloric acid solution of bromine is evaporated on a water-bath until almost all the hydrochloric acid is driven off, the residue is diluted with water, and the sulphuric acid in it precipitated by chloride of barium.

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* Compare MAX BUCHNER, Journ. f. prakt. Chem. 72, 365.

† Chem. News, 1863, No. 182, p. 254; Zeitschr. f. anal. Chem. 2, 434.

‡ Berg- und Hüttenmänn, Zeit. 1869, 52; Zeitschr. f. anal. Chem. 10, 245.

§ Chem. News, v. 22, p. 101; Zeitschr. f. anal. Chem. 10, 245,

‖ Journ. of the Chem. Soc. 23, 375; Zeitschr. f. anal. Chem. 10, 246.

¶ Eng. and Min. Journ. New York, 23, 168; Zeitschr. f. anal. Chem. 16, 504.

** Amer. Chemist, 5, 365; Zeitschr. f. anal. Chem. 16, 505.

†† Zeitschr. f. anal. Chem. 2, 46.

‡‡ *Ibid.* 13, 37.

As sulphur compounds may still be left in the insoluble residue left in dissolving the iron, this is collected, washed, dried, and fused with carbonate of potassa and nitrate of potassa over a spirit-lamp; it is then extracted with water, filtered, the aqueous solution acidified with hydrochloric acid, the whole evaporated on the water-bath, a few drops of hydrochloric acid and water added, the liquid filtered, and a solution of chloride of barium added. If a precipitate is obtained, it is collected on the same filter as the other sulphate of baryta, dried, heated to redness, and weighed. An essential condition of this determination is that neither the brominated hydrochloric acid, carbonate of potassa, nitrate of potassa, nor hydrochloric acid should contain sulphuric acid. If this is not quite certain, weighed and measured quantities must be taken, and allowance made for the small amount of sulphuric acid in them.

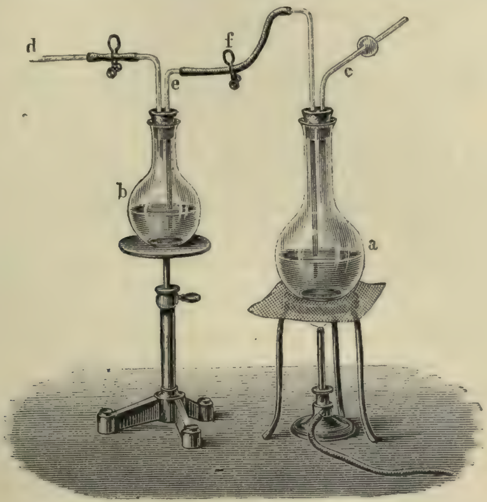

FIG. 104.

Instead of using bromine in hydrochloric acid, the hydrogen containing sulphuretted hydrogen can be passed through a solution of lead oxide in potash solution. The precipitated sulphide of lead is collected, dried, and oxidized by fuming nitric acid, and the excess of the latter removed by evaporation. The residue, together with that left undissolved by hydrochloric acid, is fused with carbonate of potassa and nitrate of potassa, moistened with water, and any traces of dissolved lead precipitated by a current of carbonic acid. After filtration, the filtrate is acidified by hydrochloric acid, evaporated on a water-bath, and the residue extracted with a few drops of hydrochloric acid and water, filtered, and precipitated by chloride of barium.

It will be easily understood that the sulphuretted hydrogen can be converted into sulphuric acid by other means. HAMILTON[*] employs caustic potash, and chlorine; DROWN,[†] a solution of permanganate of potassa; both ultimately converting the sulphur into sulphate of barium. ELLIOT[‡] uses caustic soda, and determines iodometrically the sulphide of potassium produced (§ 148). M. KOPPMAYER[§] proposes a solution of iodine in iodide of potassium and estimates the residual iodine. HIBSCH[||] has shown that this last method gives inaccurate results because the hydrocarbon also acts on iodine, and the same objection can likewise be raised against ELLIOT's method.

b. Methods for dissolving the Iron in such a manner that all the Sulphur remains in the insoluble residue.

α. GINTL's process.[¶] About 5 to 10 grams of rather finely powdered crude iron is placed in a roomy glass flask and digested for 8 to 10 hours at 25°–30° with about twenty times the quantity of a moderately concentrated solution of ferric chloride freed as far as possible from excess of acid, the flask being inclined during the operation. The greater part of the iron dissolves as ferrous chloride with gentle evolution of hydrogen, it is then diluted and the residue, consisting of the small amount of undissolved iron, carbon, graphite, all the sulphur, phosphorus, and nearly the whole of the silica, is collected, washed quickly and dried; it is then placed with the filter in a porcelain crucible, at the bottom of which is placed a layer consisting of a mixture of 3 parts of nitrate of potassa and 1 part of caustic potash (both, of course, free from sulphuric acid), and covered with another layer of the same mixture. The crucible is then heated over a spirit lamp, moderately at first, but gradually more strongly. After complete oxidation, the cold fused mass is steeped in water, filtered, acidified with hydrochloric acid, and the sulphuric acid precipitated by chloride of barium, &c. The best analyses given by GINTL do not vary very much from the results obtained by the first method (*a*). E. RICHTERS[**] and J. E. HIBSCH[††] also obtained fairly concordant results by both methods.

β. MEINEKE[‡‡] employs a process similar to that of GINTL, replacing however, the ferric chloride by an acid solution of chloride of copper, in order to avoid the inconvenient separation of basic iron salts; the action is assisted by gently warming, and the precipitated copper is finally dissolved as chloride by the addition of a solution of chloride of copper in chloride of sodium, the sulphur being determined in the residue after it has been collected and washed, first with a hot solution of chloride of sodium and subsequently with water. MEINEKE oxidises the sulphur in the wet way by nitric acid and chlorate of potassa (Vol I. p. 388); this can, of course, also be effected by fusing the residue with carbonate of soda and nitrate of potassa (Vol. I. p. 383).

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[*] Chem. News, 21, 147; Zeitschr. f. anal. Chem. 9, 508.

[†] Zeitschr. f. anal. Chem. 13, 343.

[‡] Chem. News, 23, 61; Zeitschr. f. anal. Chem. 11, 105.

[§] Dingl. polyt. Journ. 210, 184.

[||] *Ibid.* 225, 611; Zeitschr. f. anal. Chem. 18, 625.

[¶] Zeitschr. f. anal. Chem. 7, 428.

[**] Dingl. polyt. Journ. 197, 168; Zeitschr. f. anal. Chem. 10, 370.

[††] Dingl. polyt. Journ. 225, 61; Zeitschr. f. anal. Chem. 18, 625.

[‡‡] Zeitschr. f. anal. Chem. 10, 280.

c. *Methods for dissolving both the Iron and Sulphur in oxidising solvents and precipitating the Sulphuric Acid in the solution by chloride of barium.*

None of the methods of this kind where the iron is dissolved by aqua regia or bromine, or is converted by chlorine into ferric chloride in the dry way (HIBSCH), are to be recommended, as on precipitating the sulphuric acid from the solutions containing ferric chloride or bromide, some of the sulphate of baryta remains dissolved, whilst, on the other hand, the sulphate of baryta thrown down contains iron.*

3. Estimation of Nitrogen.

Nitrogen, according to the researches of BOUIS, BOUSSINGAULT, FREMY, and ULLGREN,† occurs in cast iron (steel and wrought iron) in two conditions irrespectively of what is occluded in the gaseous state (F. C. G. MULLER ‡). When the iron is dissolved in hydrochloric acid, a part of the nitrogen is converted into ammonia by the action of the nascent hydrogen, whilst another part remains in the insoluble carbonaceous residue. The methods which are here given for the determination of the nitrogen in each condition, are taken from ULLGREN'S papers,§ the most recent which have been published on this subject; in these, attention is directed to several important points which were formerly overlooked.

a. *Estimation of the Nitrogen which forms ammonia on dissolving the iron in hydrochloric acid.*

α. The iron is dissolved, in hydrochloric acid, in a flask or tubulated retort, taking care that the escaping hydrogen, which carries away a little ammonia, is passed through a U-tube containing a little dilute hydrochloric acid. When dissolution is complete, the contents of this U-tube are mixed with those of the flask, and the whole distilled with excess of hydrate of lime until half the liquid has passed over, the evolved ammonia being estimated as directed in § 99, 3, *a*.

β. About 2 grams of the finely divided cast iron is treated in a tubulated retort with a solution of 10 grams of crystallised sulphate of copper, and 6 grams of fused chloride of sodium. When the iron is dissolved, milk of lime is added and the process continued as in *a*.

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* See Zeitschr. f. anal. Chem. 2, 46 and 439; 7, 429; and 19, 53.

† Comp. Zeitschr. f. anal. Chem. 2, 435.

‡ Ber. deutsch. chem. Gesell. 14, 6.

§ Ann. d. Chem. u. Pharm. 124, 70, and 125, 40; Zeitschr. f. anal. Chem. 2, 435.

Ullgren gives preference to the latter method. If the process is conducted as in *a*, as it was formerly, the ammonia carried away by the hydrogen, some $\frac{1}{5}$th to $\frac{1}{6}$th of the whole, is lost.

b. Estimation of the Nitrogen, which remains in the carbonaceous residue on dissolving the iron.

According to **Ullgren**, if the carbonaceous residue left on dissolving the iron in hydrochloric acid is burnt with soda-lime (§ 186), as **Boussingault** recommended, the results obtained are unsatisfactory, because the graphite requires for its oxidation at the expense of the water in the hydrate of soda, a temperature far exceeding that at which it is possible for ammonia to exist. On this account it is necessary to separate the nitrogen in the gaseous state. **Ullgren** employs sulphate of mercury for the combustion, using the apparatus represented in fig. 105. *A* is an ordinary combustion tube, 30 cm. long, filled as far as *g* with about 12 grams of magnesite or bicarbonate of soda;* at *g* there is a plug of asbestos, and from *g* to *f* is the mixture of about 0·1 gram of the carbonaceous residue dried at 130°, with about 3·5 or 4 grams of mercuric sulphate as free as possible from mercurous salt, and also the small quantity of the mercury salt used for rinsing the agate mortar; an asbestos plug follows next, then a 2-inch layer of coarsely powdered pumice (*f* to *h*) which has previously been mixed with mercuric sulphate and a little water and then dried again; lastly, a plug of asbestos is pushed in. The fore part of the tube is filled with pieces of pumice which have been boiled with a concentrated solution of dichromate of potassa and allowed to cool therein. After draining, they are inserted, while still moist, into the tube; they serve to absorb the sulphurous

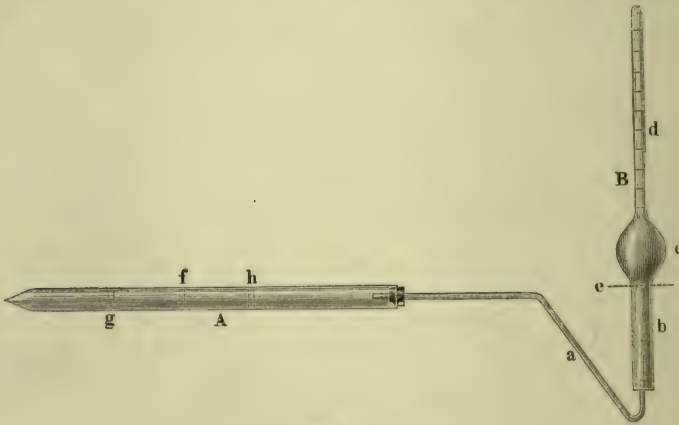

Fig. 105.

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* Since the ammonia-soda process has come into use, commercial bicarbonate of soda frequently contains ammonia, so that it is necessary to carefully test it for ammonia before using it.

acid, and act with rapidity and ease. The gas tube *a*, connected with the combustion tube *A*, dips into a mercurial trough (not represented in the cut), in which the measuring tube *B* is inverted. The narrowest part of the latter, which holds about 20 c.c., is graduated, and must be so narrow as to permit of reading off to $\frac{1}{10}$ c.c. The bulb *c* holds about 40 c.c., the lower part *b*, 20 to 30 c.c. At the commencement, this tube is completely filled with mercury and inverted, then a solution of 1 part of hydrate of potassa in 2 parts of water is allowed to run up until the bulb *c* is filled to within about 10 c.c., and lastly 15 c.c. of a clear, saturated solution of tannic acid. The mercury will now stand at about *e*. When the apparatus has been arranged and the part of the combustion tube to be heated has been surrounded with thin sheet metal, the air is driven out of the tube in the usual manner by heating one half of the bicarbonate at the hinder part of the tube, and the turned-up point of *a* is then pushed under *B*; the part *g f* of the tube is first heated gently to remove any moisture that may have been deposited, then the part between *f* and *h*, containing the pumice impregnated with mercuric sulphate, is heated,* and when this is red-hot, the mixture is raised rapidly to a bright red heat, the heating being continued until the evolution of gas ceases and the column of liquid in the measuring tube no longer descends; the rest of the carbonate is now heated. As soon as the tubes are full of pure carbonic acid, the height of the liquid in *B* remains constant. B is now transferred to a pneumatic trough, when the mercury and potash will be displaced by water, the nitrogen is measured, taking readings of the barometer and thermometer, and its weight calculated from the volume.

4. Estimation of the Phosphorus (Phosphorus, Arsenic, and Copper).

For estimating phosphorus, the iron should not be dissolved in aqua regia, a method formerly employed, because—as C. STÖCKMANN† has shown—some phosphorus compounds are volatilized,‡ and also because, when the solution contains organic matter, the precipitation of the phosphoric acid as phosphomolybdate of ammonia is not quite complete, rendering the results too low. This makes a considerable alteration necessary in the method described in the 5th edition for the estimation of phosphorus. Of the following methods, the author gives a decided preference to the first.

First Method (a modification of C. STÖCKMANN's). This also allows of the determination of *arsenic* and *copper*.

About 5 grams of the powdered cast iron is introduced into a 1-litre flask, in the neck of which a funnel is placed, and treated with 60 c.c. of pure nitric acid of sp. gr. 1·20. The acid is added by degrees, and when frothing has entirely ceased, the mixture is gently boiled until all the iron is dissolved. The contents of the flask together with the water used to rinse it out are now gradually evaporated in a porcelain dish of 160 to 200 c.c. capacity, about 5 grams of nitrate of ammonia being added towards the end; it is then evaporated to dryness, with stirring, on a sandbath, and the contents of the basin strongly heated over a bare flame to destroy all nitrates and organic matter. This is greatly facilitated by adding nitrate of ammonia, a modification introduced sometime back by the author. The residue is now digested with fuming hydrochloric acid, with application of heat, until all the ferric oxide is dissolved; the solution is then diluted, filtered, and the filtrate repeatedly evaporated with nitric acid until the hydrochloric acid is removed.* Ammonium molybdate is then added as described in Vol. I. p. 307, β.

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* The object of this layer of pumice is to prevent the otherwise possible evolution of carbonic oxide.

† Zeitschr. f. anal. Chem. 16, 174.

‡ According to the experiments made in the author's laboratory this loss of phosphorus is exceedingly small.

As, however, arsenate of ammonia and magnesia may be thrown down along with the phosphate of ammonia and magnesia, the precipitate, after being washed with water containing ammonia, is dissolved in hydrochloric acid, precipitated at 70° by sulphuretted hydrogen, and filtered from the precipitate of sulphide of arsenic and some sulphide of molybdenum. The filtrate and washings are concentrated, precipitated with ammonia and a little magnesia mixture, and after adding more ammonia, the now fully purified phosphate of ammonia and magnesia is converted into pyrophosphate of magnesia (Vol. I. p. 307).

If the arsenic and copper are also to be estimated, or if the quantity of phosphorus is very small, the process is modified in the following manner. The residue left on evaporation, and which has been heated to redness and digested with hydrochloric acid, is largely diluted and filtered (to this is also added the hydrochloric acid solution of the product obtained by fusing with carbonate of soda the residue insoluble in hydrochloric acid), and sulphuretted hydrogen is passed through it at 70°; after filtering, the filtrate is heated until the sulphuretted hydrogen is driven off, and the whole of the phosphoric acid is then thrown down, together with a small portion of ferric oxide, by the method described in Vol. I. p. 317, γ (preferably by the use of carbonate of lime). This precipitate is dissolved in nitric acid, heated to boiling and then precipitated by molybdic acid solution, &c. (Vol. I. p. 307, β).

The copper and arsenic in the precipitate produced by sulphuretted hydrogen, and consisting chiefly of sulphur, are separated as in § 164 after the greater portion of the sulphur has been removed by means of carbon bisulphide.

Second Method (ANDREW A. BLAIR †). About 5 grams of the iron are first of all treated with nitric acid as in the first method, the solution evaporated to dryness, 35 c.c. of hydrochloric acid is added, the vessel covered, and the whole heated until the iron is dissolved; the solution is then again evaporated to dryness, and heated at 120°–130° until the odour of hydrochloric acid is no longer perceptible. When cold, it is dissolved in 35 c.c. of hydrochloric acid, 50 c.c. of water is added, and the mixture boiled for half an hour to convert any pyrophosphate that may have been formed into orthophosphate; the excess of acid is then evaporated, and the silicic acid filtered off and washed, first with dilute hydrochloric acid, and finally with hot water.

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* If the residue is not white, the precaution is necessary of decomposing it with carbonate of soda, dissolving the fused mass in nitric acid, separating the silicic acid, and testing the filtrate with molybdenum solution to ascertain if any phosphoric acid is present.

† Zeitschr. f. anal. Chem. 18, 122. This method is adopted in the experimental station established by the United States of North America for the examination of iron, steel, &c.

After diluting the filtrate to about 400 c.c., acid sulphite of ammonia is added in quantity sufficient to convert the ferric chloride into ferrous chloride, and the mixture is heated to boiling and nearly neutralized with ammonia, for if the liquid is too strongly acid the reduction is incomplete. To the now colourless solution, 50 c.c. of concentrated hydrochloric acid is added, the mixture boiled until all the sulphurous acid is driven off, cooled quickly, and ammonia added to the completely cold liquid until a slight green precipitate is obtained on shaking. This is dissolved in a few drops of acetic acid, and 1 to 2 c.c. of a concentrated solution of acetate of ammonia and 3 to 5 c.c. of dilute acetic acid are added. After diluting to 750 c.c. with hot water, a very dilute solution of ferric chloride (about 7 grams of iron in 1000 c.c.) is added, and if the precipitate first produced is white, drop by drop, until the precipitate is of a dull red tinge; the solution is heated to boiling, filtered hot, and the precipitate washed quickly with boiling water, redissolved in hydrochloric acid, and evaporated almost to dryness; sufficient citric acid (about 2 to 3 grams) is added to keep all the iron in solution, then ammonia until just alkaline, ammonium magnesium chloride solution, and finally more ammonia. The quantity of liquid should not exceed 20 to 30 c.c. At the end of 12 hours, the precipitate is collected, washed with ammoniacal water, evaporated, heated to redness, dissolved in equal parts of hydrochloric acid and water, in a platinum crucible, and boiled for 30 minutes to convert the pyrophosphate into orthophosphate.* It is then filtered, concentrated to 20 to 30 c.c., 2 or 3 drops of magnesia mixture is added, a little citric acid, then ammonia, and the now pure precipitated phosphate of ammonia and magnesia is estimated as pyrophosphate. If the precipitate of phosphate of ammonia and magnesia first obtained is very small, BLAIR recommends weighing it after ignition, estimating the silicic acid in it, and making a correction for it.†

Third Method (F. KESSLER),‡ 5·6 grams of the iron, sufficiently finely broken, is dissolved in a covered porcelain basin, in 60 c.c. of nitric acid of 1·2 sp. gr., evaporated, finally with stirring, over a naked flame, and heated to redness; it is then transferred as far as possible to a platinum crucible, and heated until all the carbon is consumed. The contents of the crucible are now put back into the basin and treated with 35 c.c. of hydrochloric acid of 1·19 sp. gr., which dissolves the ferric oxide, and leaves the silicic acid. If the latter is not to be estimated, filtration is not necessary, and the ferric chloride solution is transferred along with the silicic acid to a flask, 200 c.c. of water is added, the iron completely reduced by passing in sulphuretted hydrogen, 200 c.c. of ferrocyanide of potassium solution (210 grams of the crystallized salt per litre) is added, and the volume made up to 518 c.c. (the 18 c.c. representing the space occupied by the copious light blue precipitate of potassium ferric ferrocyanide). After mixing, it is filtered through a dry filter, covering the funnel; the first portions of the filtrate, which are usually turbid, are collected separately, and then enough of the clear filtrate to fill a 250 c.c. measuring flask, 20 c.c. of magnesia mixture being added to it (Vol. I. p. 307). After 12 hours, the precipitate is collected and washed with ammoniacal water, dissolved in nitric acid of sp. gr. 1·035, the small quantity of undissolved blue ferrocyangen compound filtered off, and the filtrates re-precipitated by ammonia with addition of some magnesia mixture as described in Vol. I. p. 307. According to experiments made in the author's laboratory, this method yields results sufficiently concordant with those obtained by the first method, when employed for iron rich in phosphorus, but it is not adapted for iron containing only a small amount of phosphorus.

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* The conversion is, however, incomplete, see § 74 *c*.

† According to experiments made in the author's laboratory, this method yields results which are too low.

‡ Zeitschr. f. anal. Chem. 11, 106.

Fourth Method (Gintl's).* In this, the estimation of the phosphorus is made conjointly with that of sulphur (this vol. p. 332). For this purpose, the filtrate from the sulphate of baryta is treated with sulphuric acid to remove the excess of baryta; then supersaturated with ammonia, freed from manganese by sulphide of ammonium, and the phosphoric acid thrown down from the filtrate by magnesia mixture (Vol. I. p. 306). E. Richters † obtained in this way results which agreed to some extent with those obtained by the first method, but not satisfactorily. It is necessary above all things to test the ferric chloride solution for phosphoric acid, and advisable to dissolve the residue, left after treating the fused mass with water, in nitric acid and to test the solution with molybdic solution, as the ferric oxide may retain phosphoric acid. It is scarcely necessary to remark that the phosphoric acid can also be at once precipitated by molybdenum solution in the filtrate from the sulphate of baryta (Vol. I. p. 307).

5. Determination of the total amounts of Silicon, Iron, Manganese, Zinc, Cobalt, Nickel, Chromium, Alumina, Titanium, and also of the Metals of the Alkaline Earths and Alkalies.‡

a. General Methods.

From 5 to 10 grams of the cast iron is dissolved in moderately dilute hydrochloric acid in a covered beaker, washed into a porcelain dish,§ and evaporated on the water-bath to dryness until the mass no longer smells of hydrochloric acid; it is then moistened with hydrochloric acid, heated, water added, and the precipitate re-collected on a filter, washed, and dried; this is called *a*. The solution is divided and put into two large flasks, heated with nitric acid, diluted largely, and the ferric oxide precipitated by nearly saturating it with carbonate of ammonia and boiling, as in Vol. I. p. 437, 3 *a*; the precipitate is collected, washed somewhat, again dissolved in hydrochloric acid and the precipitation repeated again in the same manner. The precipitate is washed with water containing nitrate of ammonia, and dried; this is called *b*.

The filtrate from *b* is mixed with ammonia in slight excess, heated until the excess of ammonia is almost expelled, filtered after standing a short time, dissolved in hydrochloric acid and reprecipitated once more in the same manner. The precipitate is then collected, washed, and dried; this is *c*.

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* Zeitschr. f. anal. Chem. 7, 428.

† *Ibid.* 10, 370.

‡ Comp. Lippert, Beiträge zur Analyse des Roheisens, Zeitschr. f. anal. Chem. 2, 39.

§ If it is desired that the estimation of the silicon and aluminium should be as accurate as possible, the dissolution of the iron and the evaporation of the solution must be conducted in a platinum basin; the solution then, however, contains a little platinum, which considerably interferes with the separation and estimation of the other metals.

The filtrate from *c* is acidified with acetic acid, concentrated, made alkaline with ammonia, then again made distinctly acid with acetic acid, acetate of ammonia is added, and sulphuretted hydrogen passed through the solution at 70°. As soon as the precipitate, *d*, has subsided, it is collected.

The liquid filtered from *d*, and contained in a flask which it nearly fills, is made alkaline with ammonia, sulphide of ammonium is added, the flask is loosely stoppered, and the whole allowed to remain for twenty-four hours in a warm place. The precipitate (manganese sulphide) is *e*.

The liquid from the manganese sulphide is evaporated to dryness in a platinum dish and the ammonia salts driven off; the residue is extracted with hydrochloric acid and water, filtered, and any lime which may be present is precipitated by oxalate of ammonia, then any magnesia by phosphate of ammonia, and finally, after removal of the phosphoric acid, the potash and soda are estimated if any are present (*see* § 154, 6 and § 153, 4 *b*.*)

The precipitates, *a*, *b*, *c*, *d* and *e* are now examined.

The residue *a* contains the whole of the substances insoluble or sparingly soluble in hydrochloric acid. Besides carbon, silicic acid, and leukon, the following may be present, namely, phosphide of iron, chromium-iron, vanadium-iron, arsenide of iron, carbide of iron, silicon (?),† molybdenum, &c., and also the slag in a more or less altered condition. Titanic acid and sulphate of baryta may also be present in the residue. This is fused with carbonate of soda and potassa, and a little nitrate, the silicic acid separated as usual, by evaporating with hydrochloric acid, weighing it and examining it to see that it is pure (comp. Vol. I. p. 348), paying particular attention to titanic acid. The silicic acid may have been partly formed from silicon, and partly present as such in the slag. In the filtrate from the silicic acid, what is separable by ammonia by double precipitation should be separated, the precipitate filtered off (*c*′), and the solution feebly acidified with acetic acid; acetate of ammonia is then added, sulphuretted hydrogen passed in at 70°, and the precipitate *d*′ filtered off, the precipitate *e*′ is thrown down by sulphide of ammonium, and the filtrate finally tested for alkaline earths, any small quantities of which can then be weighed at the same time as the somewhat larger amount obtained above.

The precipitates *b*, *c* and *c*′ contain the whole of the ferric oxide and alumina, and also that part of the silicic and titanic acids which have passed into solution; the mixed ignited precipitates are transferred to several porcelain boats, and these are put into a porcelain tube and ignited in a current of pure hydrogen until no more water vapour issues. The boats containing the reduced iron are now treated with very dilute nitric acid to dissolve the iron (Vol. I. p. 441 [**91**]), the solution is made up to 1000 c.c. and the iron determined in an aliquot part by adding tartaric acid and ammonia, precipitating with sulphide of ammonium, and converting the ferrous sulphide into ferric oxide (§ 113, 1, *b*.)* The residue, insoluble in the very dilute nitric acid, is fused with acid sulphate of potassa, extracted with cold water, and filtered from any undissolved silicic acid, which must be added to that found above; sulphuretted hydrogen is then passed through the liquid, and any titanic acid which may be present is precipitated by boiling it while passing a stream of carbonic acid (§ 107); from the filtrate, or the solution if it has remained clear, the alumina is precipitated with ammonia, after boiling with nitric acid, and separated from the small quantity of ferric oxide which may possibly be present by the method given in this vol. p. 153. Here, as in the former case, regard must be paid to phosphoric acid, as its presence in the alumina would make the weight of the latter too high. If chromium were present, its oxide would likewise have to be separated and determined in this precipitate.

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* It is easily seen that the estimation of the alkalies is only of value if care has been taken to ascertain that the ammonia and ammonia salts are free from fixed alkalies, and also that all the operations have been carried out in platinum vessels.

† Compare TOSH, Zeitschr. f. anal. Chem. 5, 430.

The precipitates *d* and *d′* may contain sulphides of copper, cobalt, nickel and zinc. They are dissolved in a little brominated hydrochloric acid, heated until the excess of bromine is driven off, the copper precipitated with sulphuretted hydrogen, and the cobalt, nickel and zinc in the filtrate separated and estimated according to § 160.

The precipitates *e* and *e′* consist of sulphide of manganese; they are treated as in § 109, 2, and finally the purity of the manganese sulphide is tested after weighing it.

b. Special Methods.

a. For the estimation of the total Silicon.

aa. If the phosphoric acid is determined as in 4 (first or third method), the residue insoluble in hydrochloric acid contains the whole of the silicon as silicic acid. This can be determined by fusing it with carbonate of soda with the addition of nitrate of potassa, and proceeding according to the usual methods.

bb. THOMAS M. DROWN and PORTER W. SHIMER † recommend, in estimating the total silicon, that the cast iron should be treated with nitric acid until it is dissolved as far as possible, and then evaporated with sulphuric acid until the whole or nearly the whole of the nitric acid is driven off. It is diluted, and the residue consisting of silicic acid and carbon is collected and washed, first with water, next with hydrochloric acid and finally with hot water; it is then dried, heated to redness with free access of air, and the silicic acid weighed. As obtained in this manner it is free from titanic acid.

Another very rapid method recommended by the same authors ‡ (fusing the iron with twenty-five times its weight of acid sulphate of potassa in a very capacious platinum crucible, treating the fused mass with water, and the insoluble residue of silicic acid with hydrochloric acid and water) yields with many kinds of iron useful results, but in others they come out too high or too low; it is only suitable for approximate estimations when these have to be made very quickly.

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* It is not advisable to determine the iron in a separately weighed smaller quantity, unless the sample to be examined is perfectly homogeneous.

† Transactions of the American Institute of Mining Engineers, vol. vii. p. 346.

‡ *Ibid.* vol. viii.

β. *Estimation of Titanium.*

To estimate titanium, T. M. Drown and Porter W. Shimer * heat the iron in a porcelain boat in a glass tube in a current of pure, dry chlorine ; the glass tube must be long enough to receive all the volatilised chloride of iron. Three U-tubes containing water are connected with the further extremity of the tube to retain the volatilised chlorides of silicon and titanium. When the operation is ended, the contents of the tubes are transferred to a porcelain basin and strongly acidified with hydrochloric acid, 15 c.c. of sulphuric acid, sp. gr. 1·23 is added, and the mixture evaporated until all the hydrochloric acid is driven off. The precipitated silicic acid is now filtered off, and the titanic acid thrown down from the filtrate, after dilution with water, by boiling (§ 107). The silicon determinations made under these conditions generally came out somewhat too low.

γ. *Estimation of Iron.*

The iron contained in cast iron can of course be determined volumetrically best by dissolving about 10 grams precisely in the manner described in this vol. p. 335, 4 (First method); the solution then contains all the iron as chloride. Should it contain free chlorine, this is removed by evaporating the solution, making up the volume to 1 litre, and estimating the iron in 50 c.c. by means of stannous chloride as described in Vol. I. p. 225. A variation of the method there given is recommended by Kessler.† In this method, stannous chloride is first added until all the ferric chloride is transformed into ferrous chloride ; then an excess of chloride of mercury to convert the excess of stannous chloride into stannic chloride; next a titrated solution of dichromate of potassa until a test drop no longer gives ferrous ferricyanide on the addition of ferricyanide of potassium; and lastly a subsidiary solution of ferrous chloride until the ferrous ferricyanide reaction is again observed. By deducting from the total chromate of potassa used, the quantity corresponding with the ferrous chloride solution employed, the amount required to convert the ferrous chloride yielded by the cast iron into ferric chloride is ascertained, and from this the amount of iron can be estimated (Vol. I. p. 220, *b*).

If the cast iron contains appreciable quantities of arsenic or copper, the aforesaid volumetric methods do not yield trustworthy results. Kessler advises the following process in such cases.

The hydrochloric acid solution is precipitated at 70° by sulphuretted hydrogen, filtered, and the filtrate boiled while a current of carbonic acid is passed through it, so as to drive off the greater portion of the sulphuretted hydrogen, the remainder being removed as chloro-sulphide of mercury by the copious addition of mercuric chloride, and the solution is titrated at once with dichromate of potassa as above, without filtering off the precipitate.

δ. *Estimation of Manganese.*

As a relatively quick method of estimating the manganese in cast iron is of great importance in iron manufacture, numerous methods are recommended for effecting this object volumetrically, of which the following are the most important.

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* Transactions of the American Institute of Mining Engineers, vol. viii.

† Zeitschr. f. anal. Chem. 11, 249.

aa. F. Kessler's *Method.**

This resembles *a*, in so far that the iron is thrown down as basic ferric sulphate and this is separated from manganese; and, *b*, in that bromine water when heated with a solution of protochloride of manganese to which chloride of zinc and acetate of soda have been added, throws down all the manganese as peroxide containing zinc oxide. Required: a saturated solution of bromine in water; a solution of carbonate of soda (100 grams of the crystallised salt per litre); a solution of sulphate of soda (100 grams of the crystallised salt per litre); a solution of acetate of soda (500 grams of crystallised acetate of soda per litre); a dilute solution of acetate of soda (20 c.c. of the preceding solution made up with water to 1 litre); a solution of chloride of zinc (200 grams of zinc and no free hydrochloric acid per litre); a solution of chloride of antimony (15 grams of oxide of antimony dissolved in 300 c.c. of hydrochloric acid, sp. gr. 1·19, and made up to 1 litre with water); a solution of permanganate of potassa (3·3 grams per litre).

A suitable quantity of iron is brought into solution in the manner detailed in this vol. p. 337 (third method); the liquid is then free from organic substances, and contains all the iron as perchloride and the manganese as protochloride. To the solution, diluted to about 100 c.c. and kept in rapid rotation in a measuring flask, a solution of carbonate of soda is run in from a burette until the precipitate formed ceases to redissolve; the stream of liquid run in must not be directed against the side of the vessel but on to the outer edge of the solution. Next, hydrochloric acid of 1·01 sp. gr. is carefully added drop by drop from another burette until the liquid becomes just—but completely—clear, and this indeed after *not too short a time* and frequent shaking. It is then diluted, and for every 1 gram of iron 15 c.c. of the sulphate of soda solution is added, the flask filled up to the mark, mixed and then filtered through a dry filter into a dry flask, keeping the funnel, covered. From the filtrate, a quantity containing at most 0·11 gram of manganese is now measured off and concentrated, if necessary, to about 100 c.c.; 100 c.c. of the bromine solution, 50 c.c. of the solution of chloride of zinc and 20 c.c. of the acetate of soda solution are placed in a flask, and to the mixture is added the 100 c.c, more or less, of liquid containing manganese; this must be added in five equal portions at intervals of 15 minutes. A further 20 c.c. of acetate of soda solution is now added, and the whole heated to boiling until the odour of bromine has entirely disappeared and the liquid, in which the precipitate is suspended, has become quite colourless. The precipitate is collected on a filter, washed with the dilute solution of acetate of soda, and finally replaced together with the filter in the precipitation vessel. Chloride of antimony solution in quantities of 5 c.c. is now added to the precipitate until, after prolonged agitation in the cold, the residue of the precipitate is no longer black but brown or light brown, then 25 c.c. of hydrochloric acid is added and the liquid washed into a beaker as soon as the precipitate is completely dissolved. The solution of permanganate of potassa is now added from a burette until a reddish coloration takes place and persists for at least 6 seconds.

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* Zeitschr. f. anal. Chem. 18, 1.

By titrating an equal quantity of chloride of antimony solution with permanganate of potassa under the same conditions, the difference will give the amount of permanganate of potassa equivalent in oxidising effect to the manganese peroxide contained in the precipitate (1 equiv. $KO,Mn_2O_7 = 5MnO_2$). The amount of manganese present can thence be easily calculated. If the standard of the permanganate of potassa solution has been based on iron (Vol. I. p. 215), 10 equiv. of iron (280) correspond with 1 equiv. of permanganate of potassa (158·13) or with 5 equiv. of peroxide of manganese (217·5), containing 5 equiv. of manganese (137·5).

Kessler prefers, however, to standardise the permanganate of potassa solution exactly as above by means of a manganese solution of known strength which he prepares by dissolving a weighed quantity of manganous pyrophosphate[*] in hydrochloric acid.

The first analyses given by Kessler are very satisfactory.

bb. Volhard's *Method.*[†]

This is based on the separation of ferric oxide from manganous oxide by zinc oxide, and the volumetric determination of the manganous oxide in the filtrate by permanganate of potassa; in reference to this mode of estimation (see Vol. I. p. 206). Volhard has shown that the precipitate produced by a solution of permanganate of potassa in a hot dilute solution of manganous sulphate or manganous chloride is never pure hydrated peroxide of manganese but on the contrary always contains some manganese protoxide. If, however, a salt of zinc, lime, or magnesia is added to the solution the precipitate then contains all the manganese as peroxide along with zinc oxide, lime, or magnesia. The following equation shows the reaction :

$$3(MnO,SO_3) + Mn_2O_7 + 8\ HO = 5(MnO_2,HO) + 3(HO,SO_3).$$

A suitable amount of the cast iron containing 0·3 to 0·5 grams of manganese, is dissolved in nitric acid in a flask, evaporated to dryness in a porcelain basin, adding a little sulphate of ammonia towards the end, and heated, finally over a bare flame, until the nitrate is decomposed and all the carbon is burnt off; it is then digested with hydrochloric acid, mixed carefully with a sufficient quantity of concentrated sulphuric acid and evaporated, first on a water bath and then on a gas stove, until fumes of sulphuric acid begin to come off. It is now rinsed into a litre flask, the free acid neutralised with carbonate or acetate of soda free from manganese, and then sufficient zinc oxide, suspended in water,[‡] is added until all the iron is precipitated, that is, until the gradually deepening brown red solution suddenly coagulates and the supernatant liquid becomes milky. The flask is now filled up to the mark with water, the contents mixed, allowed to stand for a time, and then filtered through a dry filter into a dry flask. 200 c.c. of the filtrate is acidified in a flask with 2 to 4 drops of nitric acid, and heated to boiling. It is now taken away from the source of heat, and a solution of pure permanganate of potassa (about 3·8 grams per litre) is allowed to run in until the liquid assumes a permanent reddish tinge. The titration is repeated with another 200 cc. of the filtrate.

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[*] The manganous pyrophosphate is prepared by mixing a solution of 40 grams of crystallised manganous sulphate with one of 60 grams of crystallised phosphate of soda, adding hydrochloric acid until the precipitate is dissolved, und then ammonia until the liquid is alkaline. It is then cleared again by the addition of hydrochloric acid, filtered if necessary, diluted to about one litre, precipitated with ammonia, and the precipitate washed by decantation until free from chlorine ; it is then redissolved in dilute nitric acid with the addition of a little sulphurous acid, super-saturated with ammonia, cleared again with nitric acid, re-precipitated once more with ammonia, and the precipitate, after being washed by repeated decantation, is dried and heated to redness.

[†] Ann. d. Chem. und Pharm. 198, 318–354.

[‡] Volhard employs commercial zinc white. This is strongly heated to a red heat for some time in an open Hessian crucible, stirring meanwhile, and then

If the standard of the permanganate of potassa solution has been determined with iron, as in Vol. I. p. 215, it must be noted that 1 equiv. of permanganic acid transforms 10 equiv. of iron from ferrous into ferric oxide or 3 equiv. of manganese from protoxide to peroxide, corresponding with 280 of ferrous oxide or 82·5 of protoxide of manganese. The manganese standard is obtained, therefore, from the iron standard by multiplying it by $\frac{82{\cdot}5}{280} = 0{\cdot}2946$. Of course the standard of the permanganate of potassa solution can be fixed by the aid of a solution of manganese of known strength or as VOLHARD prefers, by the iodometric method (see Ann. *loc. cit.* p. 333). The test analyses given by VOLHARD are very satisfactory.

cc. JOHN PATTINSON'S *Method.**

This is founded on the following fact: If a solution of chloride of lime, or bromine water is added to a solution of protochloride of manganese containing a sufficient proportion of ferric chloride, and the mixture is heated to 60°–70° and excess of carbonate of lime is added, all the manganese goes down in the precipitate as peroxide. It is sufficient if the solution contains half as much iron as manganese, but equal parts are preferable; an excess of iron is not prejudicial. The peroxide of manganese in the precipitate is estimated by treating it with an excess of an acid solution of ferrous sulphate, and determining the excess of the latter. The reaction is shown by the equation:

$$MnO_2 + 2(FeO,SO_3) + 2(HO,SO_3) = Fe_2O_3,3SO_3 + MnO,SO_3 + 2HO.$$

For carrying out the process the following are requisite: a solution of *chloride of lime* (15 grams of good chloride of lime per litre), the clear liquid left on subsidence being used; *carbonate of lime* (prepared by precipitating chloride of calcium solution with carbonate of soda at 80°); *acid ferrous sulphate solution* containing about 10 grams of iron per litre (53 grams of ferrous sulphate are dissolved by the aid of a mixture of 1 part of hydrate of sulphuric acid and 3 parts of water, and made up to 1 litre); a solution of dichromate of potassa (see Vol. I. p. 220 *b*.) containing exactly 14·761 grams per litre. 1000 c.c. of this have the same oxidising action on a protoxide of iron solution as 13·05 grams of peroxide of manganese, and correspond with 8·25 of manganese.

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elutriated in water. A sample from the lowermost portion of the sediment is tested to see that it contains no metallic zinc; this test is performed by dissolving it in dilute sulphuric acid coloured by a drop of permanganate of potash solution. The coloration should not disappear, even on warming. The zinc oxide is kept mixed with water ready for use.

* Journ. Chem. Soc. 1879, p. 365; Zeitschr. f. anal. Chem. 19, 346.

A quantity of cast iron, containing about 0·10 to 0·15 grams of manganese is dissolved in hydrochloric acid free from organic matter (see this vol. p. 343, *bb*), carbonate of lime is added until the liquid becomes deep red, and then it is acidified again with a few drops of hydrochloric acid; about 60 c.c. of the chloride of lime solution is added, then hot water until the temperature is about 60° to 70°, and lastly some 1·5 grams of carbonate of lime. The mixture is stirred until no more carbonic acid is evolved, and then allowed to remain. If the liquid above the dark brown precipitate, which quickly settles, is reddish from permanganic acid, a few drops of alcohol are added until it becomes decolorised. The precipitate is collected on a filter, and washed with warm water until the washings when tested with iodised starch paper (this vol. p. 243) are found to be free from chlorine. An accurately measured quantity (50–60 c.c.) of the acid ferrous sulphate solution is now placed in the beaker in which precipitation was effected, and to the sides of which some of the precipitate usually still adheres, and then the filter along with the precipitate is introduced, the latter quickly dissolving.

If necessary, the mixture is diluted with cold water, and the excess of ferrous oxide titrated with the solution of dichromate of potassa (Vol. I. p. 220). In order to ascertain accurately the relation of the ferrous sulphate solution to the solution of chromate of potassa, a quantity equal to that employed must be titrated with the chromate of potassa solution, a filter[*] identical with the one used being put into the liquid. Neither lead, copper, nickel, nor cobalt should be present in the solution under examination, or at most only traces of these elements. The calculation is most easily made as follows: from the number of c.c. of chromate of potassia solution corresponding with the added ferrous sulphate solution, is subtracted that which corresponds to the ferrous oxide still remaining over. The difference indicates the quantity of chromate of potassa solution which is equivalent in oxidising action to the manganese peroxide present, and the amount of manganese is given (see above) by the equation:

$$1000 : 8{\cdot}25 : \text{the difference in question} : x$$

The test analyses given by PATTINSON are highly satisfactory.[†]

ε. *Estimation of Chromium and Aluminium.*

a. ANDREW A. BLAIR'S[‡] *Method* (greatly modified).

20 c.c. of strong hydrochloric acid diluted with 3 to 4 times its volume of water is poured on to 5 grams of iron in a half-litre flask which is closed by a rubber stopper provided with a valve opening outwards.[§] When all the iron is dissolved, the valved stopper is replaced by another, the solution is cooled, water added until the flask is three-

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[*] PATTINSON considers this precautionary measure necessary, as according to his experiments some filter papers have a slightly reducing effect, which is thus eliminated.

[†] Other methods for estimating the manganese in cast iron are given by THOM. M. CHATARD (Zeitschr. f. anal. Chem. 11, 308); CLASSEN (*Ibid.* 18, 175); C. ROSSLER (*Ibid.* 19, 75); F. BEILSTEIN and L. JAWEIN (*Ibid.* 19, 77), and others.

[‡] Americ. Journ. of Science and Arts, 113, 421; Zeitschr. f. anal. Chem. 20, 138.

[§] Dissolution can of course be also effected in a current of carbonic acid.

quarters full, and then pure carbonate of baryta until the latter is in excess, the stopper being frequently loosened. After 12 hours it is filtered, and the residue, which now certainly contains all the chromium and alumina, is washed with cold water. After fusion with carbonate of soda and nitrate of potassa, the fused mass is treated with water and hydrochloric acid, the silicic acid separated, and the hydrochloric acid solution precipitated by ammonia; the precipitate consisting of ferric oxide, alumina, and oxide of chromium is then collected on a filter, and the chromium and alumina in it determined as in Vol. I. p. 435, 2.

b. Estimation of Chromium, by R. Schöffel's* *Method.*

If an iron (for example, a chrome-iron alloy) contains not more than 8 per cent. chromium at the most, it may be dissolved by means of the double chloride of copper and ammonium (this vol. p. 319, *a aa.*), filtered, and the residue, which contains all the chromium, fused with carbonate of soda and nitrate of potassa. The fused mass is digested with water until the residue is pulverulent, so as to decompose any manganic acid which may have been formed, and is then filtered. If the solution is very poor in silicic acid, it may be carefully and exactly neutralised with nitric acid, and the chromic acid precipitated as mercurous chromate (Vol. I. p. 291, *a. β*). If, on the other hand, it contains much silicic acid, the solution is evaporated with hydrochloric acid, with the addition of a little alcohol, the silicic acid removed, and the chromium thrown down from the filtrate as hydrated oxide (Vol. I. p. 194, 1 *a*). After weighing, the chromic oxide should be tested to see that it is free from alumina; if necessary, the latter may be estimated and deducted.

If a chrome-iron alloy contains more than 8 per cent. of chromium, the treatment with the double chloride of copper and ammonium is not sufficient to dissolve the iron. In such cases it is dissolved in hydrochloric acid, filtered, and the residue fused with carbonate of soda and nitrate of potassa, the fused mass being dissolved in water and hydrochloric acid, and the solutions united. It is then neutralised almost completely, and to the still decidedly acid liquid acetate of soda is added in quantity sufficient to ensure that no free acid other than acetic acid is present; no precipitate should be formed. Bromine is now added in excess, and the liquid left for several hours in a stoppered flask, with frequent agitation; it is then boiled until the excess of bromine is driven off, carbonate of soda is added until all the ferric oxide is precipitated, and the liquid filtered; the whole of the chromium is now in the filtrate as alkali chromate, and is estimated as described above.

6. Estimation of the Metals of the Fifth and Sixth Groups.

As has been seen, the estimation of copper and arsenic can be made conjointly with that of phosphorus (see this vol. p. 335). If, however, other metals of the fifth or sixth groups are present, or the proportion of copper or arsenic is too small to be conveniently determined in 5 grams of iron, a separate and larger portion (about 20 grams) of the cast iron must be employed for the estimation of the metals of the fifth and sixth groups. This is dissolved in nitric acid, evaporated, after adding 32 c.c. of pure sulphuric acid, until all the nitric acid is driven off, diluted and filtered. The insoluble residue is fused with some carbonate of soda and nitrate of potassa, the fused mass extracted with water, sulphuric acid added, the whole evaporated until the nitric acid is driven off, and then diluted and filtered; the two sulphuric acid solutions are now united, and boiled with acid sulphite of ammonia until the bulk of the ferric oxide is reduced; the solution is then precipitated with sulphuretted hydrogen, at 70°, and the precipitate freed, if necessary, from sulphur by treatment with bisulphide of carbon. The copper, arsenic, and other metals of the fifth and sixth groups present are then separated and estimated in the insoluble residue, in the manner described in § 164 and 165.

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* Ber. deutsch. chem. Gesell. 12, 1863.

7. Estimation of Tungsten.

As tungsten, if present, cannot be estimated in the manner prescribed in 6, a separate portion must be taken for this purpose. R. Schöffel* recommends one of the following methods:

a. The very finely divided iron, or tungsten iron alloy, is treated with the double chloride of copper and ammonium (this vol. p. 319, *a*, *aa*), filtered, and the residue fused with carbonate of soda; it is then dissolved in water, filtered, nearly neutralised with nitric acid, precipitated with mercurous nitrate, collected, dried, and heated to redness. The residue of tungstic acid containing silicic acid is weighed, fused with acid sulphate of potassa, the fused mass treated with water, the residual silicic acid determined, and its weight deducted from the weight first obtained. When chromium also is present, the tungstic acid contains oxide of chromium, and the two must therefore be separated.

b. The iron or alloy in a finely divided state is treated with aqua regia until all action ceases, and the solution is then diluted and allowed to remain for a day or two; all the tungsten, including that portion originally dissolved, will be found in the insoluble residue. This is collected, dried, heated to redness, at first with access of air, then fused with carbonate of soda, and subsequently treated as in *a*.

8. Estimation of Vanadium.

Should an iron, which is rarely the case, contain vanadium, this must be estimated in a large quantity, which for this purpose is treated with dilute sulphuric acid until there is no longer any action; the solution is then filtered, the residue dried, and fused with one part of carbonate of soda and two parts of nitrate of potassa, extracted with water, and the vanadium estimated in the fused mass by the method described in this vol. p. 311, 15.

9. Estimation of the slag contained in Cast Iron, that is, the Silicon, Aluminium and the Metals of the Alkaline Earths and Alkalies which as such are combined with the Iron.

Cast iron not infrequently contains a small quantity of slag, the estimation, and determination of the composition of which are not without value, as it can only be decided, after obtaining a knowledge of them, what part of the silicon, aluminium, calcium, magnesium, potassium, &c., are contained in the metallic iron. The preceding methods give the total amounts of these elements, and the analysis of the adhering slag shows the proportions present in an oxidised condition, the difference being the amounts present combined with the metallic iron.

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* Ber. deutsch. chem. Gesell. 12, 1866.

For estimating the slag and slag constituents, the following methods are employed :

a. Heating the Iron in a current of Chlorine.[*]

A weighed quantity (about 5 grams) of the pulverised cast iron is heated in a porcelain boat inserted into a glass tube, in a current of thoroughly dry chlorine, free from air and hydrochloric acid, such as is obtained when the air is driven out of the apparatus by carbonic acid before beginning the operation, and by passing the chlorine coming from the generating flask first through a U-tube filled with lumps of peroxide of manganese, and then through a sulphuric acid apparatus. The heating is continued until no more of the ferric chloride or chlorides of silicon, sulphur, phosphorus, &c., are volatilised. In order to prevent the apparatus from being stopped up, and any inconvenience arising from the excess of chlorine, the glass tube should be sufficiently long to contain all the ferric chloride, and the exit connected by india-rubber and glass tubing with a carboy containing hydrate of lime. When cold, the contents of the boat are treated with water to remove all the soluble portions (manganous chloride, chloride of calcium, &c.), dried, and heated to redness in a current of oxygen until all the graphite is consumed. For greater security it is again heated to redness, first in a current of hydrogen, and then in a current of chlorine, after which the mass is again extracted with water, reheated in oxygen if necessary, the slag residue weighed, and its constituents ascertained. If the slag produced at the same time as the cast iron is available, it is preferable to analyse this, to determine the silicic acid in the slag residue from the iron, and from this by a comparison with the analysis of the slag to determine the other ingredients of the slag. The reason why this method is preferable, is that the slag may be attacked to some extent by pure dry chlorine, so that appreciable quantities of chloride of calcium, &c., can be extracted by water. The slag residue then no longer contains the whole of the lime, &c., which was in the slag, although all the silicic acid is left.

b. Treating the Iron with Solvents.

It will be readily recognised that the solvent must be so chosen that whilst the iron is dissolved the slag will either not be attacked, or only as little as possible. The following solvents may be employed :

Very dilute hydrochloric acid assisted by a galvanic current,[†] iodine or bromine in presence of water,[‡] or solution of mercuric chloride.[§] The residue left after dissolving the iron contains, or may contain, the combined carbon, graphite, leucon, slag, &c. It is now requisite, if the first solvent has been employed, to burn off the combined carbon and graphite, but if this is done, silicic acid may be introduced into the slag (EGGERTZ, *loc. cit.*, p. 501). It is therefore better to first remove the silicic acid and the leucon by heating the residue with a saturated solution of pure carbonate of soda, extracting with water, and burning off the carbon. In order to remove the last traces of ferric oxide, nothing more is necessary than to heat to redness first in a current of hydrogen, and finally in a current of chlorine. The residue is extracted with water, heated repeatedly with a solution of carbonate of soda, again thoroughly washed with water, and weighed. If mercuric chloride has been employed as the solvent, the mercurous chloride produced must, after washing the residue with water, be removed by the aid of chlorine water free from hydrochloric acid, or by bromine water. It follows, therefore, that the methods mentioned under *b* are no simpler and less exact than those described under *a*, so that the preference should be given to the latter.

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[*] See the author's memoir, "Beiträge zur Analyse des Roheisens," Zeitschr. f. anal. Chem. 4, 72.

[†] Lippert, Zeitschr. f. anal. Chem. 2, 48.

[‡] V. Eggertz, Zeitschr. f. anal. Chem. 7, 500.

[§] H. Rose, Handb. d. anal. Chem., 6th ed. by R. Finkener, vol. ii. p. 757.

II. STEEL AND WROUGHT IRON.

Steel as well as wrought iron usually contains the same constituents as cast iron, but as a rule a far smaller proportion of those elements which are in combination with the iron. Thus the total carbon in steel varies between 2·0 and 0·65 per cent. and in wrought iron from 0·60 to 0·016 per cent., the maximum percentage of silicon in both steel and wrought iron being about 0·6 per cent., and so on. The following elements usually form the subject of quantitative estimation in both: Carbon (chemically combined, and also in mechanical admixture, when the latter is present), silicon, sulphur, phosphorus, manganese, and copper. When large quantities of wrought iron or steel are treated, other elements such as nickel, cobalt, arsenic, tungsten, &c., may also be estimated quantitatively.

Although the methods are, on the whole, identical with those for cast iron, the addition of a few supplementary remarks may be useful.

1. Estimation of Carbon.

a. If unhardened steel is dissolved slowly and without warming in dilute hydrochloric or sulphuric acid, a carbonaceous residue is left (CARON,* RINMANN†), whereas the same unhardened steel leaves no carbonaceous residue if it is dissolved by heating it with hydrochloric acid of sp. gr. 1·12, and is then boiled for half an hour or so after dissolution is complete. The same steel in the hardened state leaves no residue when dissolved in cold dilute acid, so that the carbon in the said carbonaceous residue cannot be graphite; RINMANN calls it "cementkohle" (cement carbon). DEBRUNNER‡ arrived at a similar result, namely, that in steel, and generally in various kinds of iron, the carbon may also be present in a third condition differing from graphite and from combined carbon. He found, namely, that by dissolving cast steel (crucible or Bessemer steel) in nitric acid of sp. gr. 1·20, a brown flocculent precipitate was produced which disappeared on heating. By similar treatment of welding steel (puddled or cementation steel) on the other hand, a black velvety powder separates which, although resembling graphite in appearance, likewise completely dissolves on heating. **Debrunner** calls the carbon thus obtained from welding steel, semi-combined carbon, and uses the different behaviour of steels on dissolution in nitric acid as a means of distinguishing between them. It should be noted in reference to the results of these investigations that it ought not to be assumed without further inquiry that the carbon which separates when steel or wrought iron is dissolved in cold dilute hydrochloric or nitric acids, is graphite. Rather, a carbon can only be considered to be a graphite if, on separating out when an iron is rapidly dissolved in hot hydrochloric acid, it does not redissolve either on continued boiling of the liquid or by subsequent treatment with alkali and with alcohol. Whether the amount of the so-called "cement carbon" (semi-combined carbon) can be accurately estimated by dissolving steel or wrought iron in cold dilute hydrochloric acid, whereby it is left undissolved together with the graphite, requires further comprehensive investigation.

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* Compt. rend. 1863.

† Zeitschr. f. anal. Chem. 4, 159; 7, 499.

‡ Iron, 12, 775; Ding. polyt. Journ. 231, 475; Zeitschr. f. anal. Chem. 18, 624.

b. The method most frequently employed for estimating the total carbon in steel and wrought iron is the treatment with copper salts (this vol. pp. 319–320) and the conversion of the separated carbon into carbonic acid by burning it in a current of oxygen or by means of chromic acid (this vol. pp. 323–327). As the proportion of carbon is always considerably smaller than in cast iron, 5 to 10 grams are taken for this purpose.

c. If **Weyl**'s method (this vol. pp. 320–322) is employed to dissolve the steel or wrought iron, the modification described on p. 321, and the apparatus represented in fig. 101 must be employed, otherwise the results obtained will be too low as explained on p. 321. Compare **Rinnmann**,* **Schnitzler**,† and **Weyl**.‡

d. **Eggertz**' colorimetric method (this vol. p. 330) is very useful for approximately estimating the combined carbon, especially in steel works where similar raw materials are continuously used and the steel differs merely in the amount of carbon. This process has been considerably modified by **Gruner**,§ J. B. **Britton**,|| and **Morrell**.¶

2. Determination of the other Constituents.

In regard to these, it need only be noted, in addition to what has been already stated in § 255, that the amount of iron taken for the analysis must be correspondingly increased, having regard to the very same amount of the other elements combined with it.

C. Pyrites.

§ 256.

Pyrites, which is now almost exclusively used for the production of sulphuric acid, is in consequence very frequently subjected to chemical analysis especially as the small percentage of copper and small quantities

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* Zeitschr. f. anal. Chem. 3, 336. † *Ibid.* 4, 78. ‡ *Ibid.* 4, 157.

§ Berg- und Hüttenmänn Zeit. 1869, 52.

|| Chem. News, 22, 101 ; Zeitschr. f. anal. Chem. 10, 245.

¶ Amer. Chemist. 5, 365 ; Zeitschr. f. anal. Chem. 16, 305.

of silver and gold present can be advantageously extracted from the burnt pyrites. In analysing pyrites, the following constituents have generally to be taken into consideration. *Sulphur*, *Selenium*, *Sulphuric Acid*, *Iron* as sulphide (mostly FeS_2) and occasionally as oxide or suboxide, *Copper*, *Zinc*, *Lead*, Bismuth, Thallium, Cobalt, Nickel, *Arsenic*, Antimony, *Lime*, *Magnesia*, *Carbonic Acid*, the portion insoluble in acids (*Gangue*) occasionally containing *sulphate of Baryta* and Carbon, and the *Water* of combination. In many pyrites—notably the Spanish—traces of Silver and Gold are found. As a rule, even in complete analysis, only those constituents which are printed in italics are quantitatively determined.

I. COMPLETE ANALYSIS.

The mineral, very finely ground, is dried at 100°.

I. Estimation of Sulphur, Sulphuric Acid, and Arsenic; testing for Antimony.

One gram of the powdered pyrites is thoroughly mixed with 10 parts of an intimate mixture of 2 parts of pure carbonate of potassa and 1 part of pure nitrate of potassa in a capacious platinum crucible. The whole is covered with a layer of the above mixture, and gradually heated over a Berzelius' spirit-lamp* to the fusing point, at which it is kept for some time. When cold, the crucible and its contents are placed in a glass beaker, water is added, and heat applied until all the soluble portions are dissolved. In the case of pyrites containing lead, carbonic acid is passed into the mixture in order to precipitate the small amount of lead oxide which is held in solution by the caustic potash. The solution is then poured through a filter into a 500 c.c. measuring flask, the residue boiled with a solution of pure carbonate of potassa, filtered, and washed with boiling water, to which some carbonate of potassa has been added, until no more sulphuric acid can be detected in the washings. It is then allowed to cool, filled up to the mark, and mixed by agitation.

a. 250 c.c. of the alkaline liquid is mixed, in a large flask, with 30 c.c. of pure concentrated hydrochloric acid of sp. gr. 1·15, the strongly acid solution warmed until the carbonic acid is driven off, evaporated to dryness in a porcelain basin, 5 c.c. of concentrated hydrochloric acid added, and the whole again evaporated so as to free it from nitric acid. The residue is moistened with 2 drops of concentrated hydrochloric acid, water is added, and heat applied; the hot solution, after filtering, is precipitated by a hot solution of chloride of barium added in moderate excess.

After settling, the precipitate is collected, thoroughly washed with boiling water, dried, and the filter incinerated apart; the precipitate is then added to it, and the whole heated to redness and weighed. It is now moistened well with hydrochloric acid in a platinum crucible, water is added, and the whole heated and run through a small filter, this operation being repeated three times; the filtrate is evaporated almost to dryness on a water bath with a few drops of chloride of barium, extracted with water, filtered through the small filter and washed, the small filter is then burned in a platinum spiral over the platinum crucible in which the bulk of the sulphate of baryta, which in the meantime has been dried, is contained, and the whole ignited and weighed. The weight thus obtained usually differs by a few milligrams only from that first obtained, and is to be regarded as the true one.

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* If coal-gas, containing sulphur, is employed, the amount of sulphuric acid in the fused mass is thereby increased, and an error introduced (PRICE, Zeitschr. f. anal. Chem. 3, 483.

If the mixture of carbonate of potassa and nitrate of potassa, the carbonate of potassa solution, or the hydrochloric acid is not quite free from sulphuric acid, the small amount of sulphuric acid in these reagents must be determined, working with weighed, or measured, quantities, and before reckoning the sulphur the small quantity of sulphate of baryta which corresponds with the sulphuric acid in the reagent or reagents must be deducted from the total sulphate of baryta.

This method of estimation gives of course the total amount of sulphur in the pyrites. In order to ascertain the amount of *sulphur in combination with the heavy metals*, the sulphur existing as *salts of sulphuric acid*, if any such are present in the pyrites, must be deducted from the total sulphur. If the only sulphate present is sulphate of baryta, its amount is ascertained from the baryta in the residue of the fused mass; this is estimated by dissolving in hydrochloric acid the residue left undissolved on treating the melted mass with water, neutralising any too great excess of acid with ammonia, and throwing down the baryta from the solution, now containing but a moderate amount of free hydrochloric acid, by sulphuric acid (Vol. I. p. 182). The sulphate of baryta thus obtained contains some ferric oxide. If the amount of this is large, it must, in order to obtain an accurate result, be fused with carbonate of soda, and the melted product treated with boiling water. This allows the choice of estimating the ferric oxide in the residue, or the sulphuric acid in the solution.

If other sulphates (sulphate of lime, ferrous sulphate, &c.) are present, their content of sulphuric acid is estimated by repeatedly extracting another larger sample of the pyrites with dilute hydrochloric acid in a current of carbonic acid, and precipitating the filtrate with chloride of barium (Vol. I. p. 299) after neutralising the greater part of the excess of acid by ammonia.

b. The remaining 250 c.c. is evaporated with pure sulphuric acid, on the water-bath, until all the nitric acid is driven off, the residue is extracted with water acidified with hydrochloric acid, and sulphuretted hydrogen in large excess is passed at first for some time through the liquid heated to 70°, and afterwards in the cold. If a precipitate is produced, it is allowed to settle at a moderate temperature, collected on a small filter which has been dried at 110°, weighed, and thoroughly washed—preferably with the aid of the water-pump—by filling up the filter eight times with alcohol, four times with carbon bisulphide, and finally again three times with alcohol. After drying at 110°, it is weighed, and the precipitate calculated as pentasulphide of *arsenic* (BUNSEN).* After weighing, this can be tested for *antimony*, which is, as a rule, either not present at all or only in unweighable quantities. If it has to be determined, the method recommended by BUNSEN (see previous reference) may be chosen. In that case, the still moist sulphide on the filter, not yet treated with alcohol and carbon bisulphide, is mixed with an excess of a solution of pure caustic potash (purified by alcohol) and chlorine passed into the solution, to which the concentrated washings have been added, until all the alkali is decomposed. It is now heated on the water-bath, considerable excess of concentrated hydrochloric acid is added gradually and carefully (to prevent loss by spirting), and the liquid evaporated to one-half; the evaporated portion is then replaced by an equal volume of concentrated hydrochloric acid and again evaporated to one-half or a third, so as to remove all free chlorine. It is now mixed with very dilute hydrochloric acid, freshly prepared, *saturated* sulphuretted hydrogen water is added (100 c. c. for every decigram or less of the expected antimonic acid), and after waiting a short time until the precipitate of pentasulphide of antimony has entirely settled, a strong current of air, filtered through cotton-wool, is blown into the liquid from the blowpipe bellows, in order to remove the excess of sulphuretted hydrogen, the beaker being kept covered with a perforated watch-glass. After fifteen to twenty minutes, the precipitate is transferred to a weighed filter, washed with alcohol and carbon bisulphide as previously prescribed for sulphide of arsenic, dried at 110°, and the pentasulphide of *antimony* weighed. The filtrate containing arsenic is heated on a water-bath after adding a *few drops* of chlorine water, and the *arsenic* estimated as described above. If it is a question of the complete separation of the two metals, the antimony sulphide, before being washed with alcohol and carbon bisulphide, is dissolved in caustic potash, and the separation repeated in the manner prescribed.

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* Ann. d. Chem. 192, 305; Zeitschr. f. anal. Chem. 18, 266.

If the *arsenic* alone is to be estimated, the alkaline solution of the fused mass may, according to F. MUCK,* be treated as follows: It is acidified, and enough ferric chloride solution added to yield with ammonia a red-brown precipitate, that is one which contains an excess of ferric oxide, any great excess being removed by the addition of ammonia. It is now warmed until the precipitate has settled, and this is collected, washed, dissolved in hydrochloric acid, reduced by sulphurous acid, and the excess of the latter boiled off; the solution is precipitated with sulphuretted hydrogen, the sulphide of arsenic oxidised with fuming nitric acid, *concentrated strongly*, and the arsenic acid precipitated by magnesia mixture, &c. (Vol. I. p. 283).

2. Determination of the Iron, Copper, Lead, Zinc, &c., as well as of the Residue Insoluble in Acid.

Two to three grams of very finely powdered pyrites is digested with aqua regia until it is completely decomposed and all the sulphur is dissolved; it is then evaporated repeatedly with hydrochloric acid to remove the nitric acid, water is added, and the mixture filtered through a tared filter which has been dried at 100°. The insoluble residue, after being washed by decantation and filtration, is exhausted, if it contains sulphate of lead, by repeatedly boiling it with a solution of acetate of ammonia, and then well washed. The filter containing the residue is now dried at 100°, weighed, and the filter incinerated, and again weighed. The difference in weight between the dried and ignited residues gives the *water* of combination in the residue, and if the latter is blackish, also the amount of carbon. If sulphate of baryta has been found in 1, the amount of it is deducted from the ignited residue and the difference is calculated as *gangue*, unless for some special reason the residue is to be submitted to further analysis. If the residue contains sulphate of lead, the *lead* is precipitated from the solution in acetate of ammonia by sulphuretted hydrogen, the sulphide of lead is dissolved in nitric acid, after washing, and the lead estimated as sulphate (Vol. I. p. 244). The hydrochloric acid solution is treated with sulphuretted hydrogen at 70°, filtered, and the precipitate, after being exhausted with warm sulphide of sodium solution, is dissolved in nitric acid and any *lead* which may be present is removed by evaporating with sulphuric acid; ammonia is now added until nearly neutral, then carbonate of ammonia in sufficient excess, and the whole, after being warmed, and filtered if necessary (a precipitate may contain *bismuth*), is acidified, precipitated by sulphuretted hydrogen, and the *copper* estimated as sulphide (Vol. I. p. 257).

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* Zeitschr. f. anal. Chem. 5, 312.

The liquid filtered from the sulphuretted hydrogen precipitate is concentrated, oxidised by heating with nitric acid, and the iron separated as described in this vol. p. 300. The filtrate is acidified with acetic acid, and ammonia added in slight excess. If a slight precipitate of hydrated ferric oxide is produced, perhaps also of hydrated oxide of alumina, this is filtered off, redissolved in hydrochloric acid, reprecipitated by ammonia, the ammoniacal filtrate acidified with acetic acid, acetate of ammonia added, and the solution precipitated by sulphuretted hydrogen at a temperature of 70°. Any precipitate which may be produced is sulphide of *zinc*, frequently with some sulphides of *cobalt* and *nickel*. It is best weighed first in this state (Vol. I. p. 200, 2), and the small quantity of sulphide of cobalt and nickel estimated in the not quite pure sulphide of zinc, which in this case can be effected with sufficient exactness by treating with dilute hydrochloric acid and determining the small residue left undissolved.

Manganese is removed from the filtrate from the sulphide of zinc, &c., by means of ammonia and sulphide of ammonium. The filtrate is finally evaporated to dryness, heated to redness, and the *lime* and *magnesia* estimated in the residue, if there is any.

The precipitate containing the ferric oxide, that is the united precipitates, in which alumina may also be present, is dissolved in hydrochloric acid, the solution made up to 500 c.c., the *iron* and *alumina* estimated in 100 c.c. by precipitation with ammonia, and the *iron* volumetrically in 100 to 200 c.c. by stannous chloride (Vol. I. p. 225), or gravimetrically as in Vol. I. p. 435, 2.

3. Estimation of any Carbonic Acid which may be present.

This is effected by heating a suitable quantity of the finely ground pyrites with very dilute hydrochloric acid, and passing the gas first through chloride of calcium tubes, then through tubes containing pumice and sulphate of copper, and finally through weighed soda-lime tubes. The increase in weight of the latter gives the amount of carbonic acid evolved. For the method of proceeding see this vol. p. 233, d.

4. Estimation of the Oxygen Compounds of Iron which may be present.

If a pyrites yields any ferrous sulphate to water, or any ferric or ferrous oxide when treated with cold dilute hydrochloric acid without simultaneously evolving sulphuretted hydrogen, the oxygen compounds of iron in the said solution can be directly determined (Vol. I. pp. 214 and 222). If, however, this is not the case, the *direct* estimation of the oxygen compounds of iron must be abandoned and their presence determined by calculation.

5. Testing for Gold and Silver.

A larger quantity, say 500 grams, of the pyrites, is roasted, preferably in a muffle, failing which an inclined, open Hessian crucible can be used, until sulphurous acid ceases to be evolved; it is then finally heated to a bright red heat. The residue is powdered, and exhausted first with hot water testing the filtered extract by a few drops of hydrochloric acid to see if it contains silver; if any slight precipitate of chloride of silver separates after long standing, this is collected (Precipitate I.). The residue left after exhausting with water is digested in the dark for a long time with bromine water,* filtered with exclusion of sunlight, and the solution, to which a few drops of hydrochloric acid is added, is evaporated until all the free bromine is expelled and the liquid measures about 200 c.c. To this solution, often green from the presence of copper salts, a clear solution of ferrous sulphate is added, sulphuretted hydrogen is then passed through the warm mixture, and the whole is left for at least 24 hours, when the precipitate is collected on a filter, washed, and dried (Precipitate II.). The residue which has been extracted with bromine water is heated for a considerable time with a concentrated solution of chloride of ammonium to dissolve any bromide of silver present, filtered while still hot into a flask, and washed with hot chloride of ammonium solution; a few drops of mercuric chloride solution † is first added to the clear liquid, then a little ammonia until it is distinctly alkaline, finally sulphide of ammonium until there is excess. The flask is loosely corked and left in a warm place until the precipitate has completely settled, when it is collected on a filter, washed, and dried (Precipitate III.).

The precipitates I. II. and III. are heated under a good draught until the filters are burned and the mercuric sulphide is volatilised, the residue, containing the whole of the gold and silver present in the burnt pyrites, being ground with some dehydrated borax; the whole is then placed in a scorifier, the requisite quantity of lead added, and the mixture treated as described in this vol. p. 366. The gold in the button of gold and silver, obtained in cupellation, is estimated, after weighing, as described in Vol. I. p. 476 **(169)**. The silver present is given by difference.

6. Examination for Thallium.

Thallium may often be discovered in pyrites by simply putting some of the powdered ore on the moistened end of a platinum wire and holding it in the flame of the spectroscope; the characteristic, intensely green thallium line coincident with Ba δ flashes out transiently. If finely-powdered thalliferous pyrites is heated to redness in a tube, excluding the air as far as possible, sulphide of thallium sublimes along with the sulphur; by allowing this sublimate to burn away almost entirely in a loop of platinum wire, and then testing the residue in the spectroscope, the green line will appear very distinctly.

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* The use of bromine water or tincture of iodine for the extraction of gold was first recommended by Skey (Chem. News, 22, 245; Zeitschr. f. anal. Chem. 10, 221) in place of chlorine water as formerly employed.

† Mercuric chloride is added merely with the object of promoting the deposition of the usually very slight precipitate of sulphide of silver.

Thallium may also, according to **Crookes** and **Böttger**, be detected with great delicacy in the wet way. The powdered ore is dissolved in hydrochloric acid, with the addition of the smallest possible quantity of nitric acid, boiled with sulphite of soda until the ferric oxide is reduced, and then one or two drops of iodide of potassium is added. If thallium is present, a light yellow precipitate of iodide of thallium is formed. It is advisable to test it in the spectroscope to make sure.

II. ESTIMATION OF SULPHUR ALONE.

1. In the dry way, by weighing the sulphur as sulphate of baryta.

Although this has been already minutely and completely described in A, 1, the subject is here again referred to to note that in estimating the sulphur alone, it is best to mix 0·5 gram of the pyrites dried at 100°, with 10 parts of a mixture of 2 parts of dry carbonate of soda* and 1 part of nitrate of potassa, covering the whole with a layer of the same mixture, and to make use of a solution of pure carbonate of soda for extracting the residue insoluble in water. In other respects, the operation is carried out exactly as described above; the testing of the reagents for the presence of sulphuric acid should never be omitted; also, when it is a question as to the amount of sulphur in combination with the heavy metals, the amount existing in the form of sulphates, if any, must be deducted from the total sulphur obtained.

B. **Deutecom** † recommends the employment of a mixture containing chlorate of potassa instead of the mixture of nitrate of potassa and carbonate of soda. He heats 1 gram of pyrites with 8 grams of a mixture of equal parts of chlorate of potassa, carbonate of soda, and chloride of sodium, in a large covered porcelain crucible, at first slowly until completely dry, then strongly until uniformly fused. When cold, the mass is treated with boiling water, transferred together with the precipitate into a measuring flask, allowed to settle, and the sulphuric acid determined in aliquot parts of the clear solution. **Fr. Bockmann** ‡ recommends somewhat different proportions, namely: 0·5 gram of pyrites (or 2 grams of burnt pyrites) and 25 grams of a mixture of 6 parts of carbonate of soda with 1 part of chlorate of potassa.

2. Wet method, in which the sulphur is weighed as sulphate of baryta.

This method consists in treating the powdered pyrites with aqua regia, or with hydrochloric or nitric acid with the addition of chlorate of potassa or a similar oxidising agent, so that all the sulphur in combination with metals may be converted into sulphuric acid; the latter is then precipitated by chloride of barium from the solution in which the

* Carbonate of soda can be used in this instance instead of carbonate of potassa, as antimony need not be considered.

† Zeitschr. f. anal. Chem. 19, 313.

‡ *Ibid.* 21, Heft 2.

iron is present as ferric chloride or as ferric salts. In the "Zeitschrift für analytische Chemie," 19, 53, the author published an exhaustive criticism of these methods, showing that they contain two sources of error, yielding on the one hand a more or less red sulphate of barium containing ferric oxide; and on the other hand that the sulphate of barium is not completely precipitated, a part remaining dissolved in the acid liquid containing ferric chloride. These two sources of error act in opposite sense and counterbalance one another more or less completely.

As a rule, the following observations may be made in reference to this. An increased proportion of free hydrochloric acid and quick filtration increase the proportion of sulphate of baryta left in solution, and diminish its content of iron, whilst a smaller amount of free hydrochloric acid and filtration after long standing diminish the loss of sulphate of baryta but increase the amount of iron carried down. A suitable and equal dilution of the liquid to be precipitated is therefore presupposed. As a rule, the results obtained in this way are too low.

Lunge[*] in consequence of the author's criticism of the wet methods previously recommended by him,[†] somewhat modified the process, and he considers the estimation of sulphur in the wet way is best carried out as follows:

a. If economy of time has more to be considered than absolute exactness.

About 0·5 gram of the very finely powdered and bolted mineral is placed in an Erlenmeyer flask or a spacious glass beaker, the former being covered by a funnel, and the latter with a watch glass, and 50 parts of aqua regia is poured on to it, consisting of 1 part of fuming hydrochloric acid and 3 to 4 parts of nitric acid of sp. gr. 1·36–1·40. If the action does not immediately set in, the mixture is warmed moderately on a water bath in a good draught cupboard until a brisk action begins, when the vessel is at once removed from the water bath. As soon as the action becomes very feeble, the flask or beaker is again replaced on the water bath. The decomposition is generally complete in about ten minutes at the outside; if, however, it should not be complete even after long-continued warming, some more aqua regia must be added and the whole warmed again. If the object is not then completely accomplished or if sulphur has separated, the operation must be repeated with material which has been more finely powdered.

The whole is now evaporated to dryness with excess of hydrochloric acid, most safely on a water bath, by which means the nitric acid is removed, and any silicic acid which had become soluble is again rendered insoluble; the residue is once more moistened with a little hydrochloric acid and heated, notice being taken whether the gases of aqua regia are evolved; should this be the case, the evaporation is repeated with more hydrochloric acid until the object is accomplished. After the free hydrochloric acid is almost entirely removed by evaporation, 3 or 4 drops of concentrated hydrochloric acid are added, the mixture warmed, 100 c.c. of water added, and the whole filtered, heated to boiling, and precipitated with a boiling solution of chloride of barium of known strength (1 : 10), so that the latter is somewhat in excess. It is then removed from the lamp and the precipitate allowed to settle twenty to thirty minutes; the supernatant liquid is decanted through a filter, and the precipitate washed four times in succession by decantation with 100 c.c. of boiling water each time, moistening the precipitate in the precipitation glass with 2 c.c. of normal hydrochloric acid (this vol. p. 180) each time before adding the water. The precipitate is transferred to the filter, thoroughly washed and heated as in this vol. p. 351, *a*. The precipitate remains more or less reddish even after purification.

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[*] Zeitschr. f. anal. Chem. 19, 421.

[†] Lunge, Handbuch der Sodaindustrie, vol. i. p. 92.

b. If a high degree of precision is more important than saving time.

The decomposition and evaporation with hydrochloric acid is carried out as in *a*, the residue is treated with a little hydrochloric acid, water added, and then ammonia in not too large an excess to the moderately warm liquid; it is filtered after about ten minutes, and the hydrated ferric oxide thoroughly washed until a sample of the filtrate no longer yields any turbidity with chloride of barium even after standing a short time. The filtrate and washings are very slightly acidified with hydrochloric acid, and after being heated to boiling, hot chloride of barium solution is added in moderate excess; the precipitate is washed first by repeated decantations and then on the filter, and heated to redness. Under these circumstances, as no salts of the fixed alkalies are present, the purification by treatment with hydrochloric acid, &c., can be more quickly effected. The results of method *b* according to LUNGE's experiments gave 0·18 per cent. more sulphur than was obtained by method *a* (p. 358).

It is essential in these wet methods to test the reagents employed, especially the acids, to see that they are free from sulphuric acid. This test can only be accurately carried out by completely evaporating the acids, finally on a water bath, placing a little water in the basin and testing the solution with chloride of barium.

It is noteworthy that by these wet processes any sulphate of baryta which may be present, is as good as completely excluded from the sulphur—on the other hand sulphate of lime goes partly, and if the amount is not very large, entirely, into solution. The sulphur of the galena is only reckoned in to the very smallest extent, as the greater part of the sulphate of lead produced remains undissolved.

3. Technical method for indirectly (alkalimetrically) estimating the sulphur in the wet way.

a. PELOUZE'S *Method.*[*]

1 gram of the *very finely-powdered* ore is mixed with about 5 grams (exactly weighed) of perfectly pure and anhydrous carbonate of soda,[†] 7 grams (approximately weighed) of chlorate of potassa is added, and 5 grams[‡] (approximately weighed) of fused, or at least anhydrous

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[*] Comp. rend. 53, 685; Zeitschr. f. anal. Chem. 1, 249.

[†] If this is not at hand, the experiment can be performed with carbonate of soda which is not quite pure; in this case, however, the amount of normal acid which corresponds with the 5 grams, must be determined by a special experiment.

[‡] The amount of common salt may be varied for different specimens of pyrites, and may be increased until the oxidation takes place without deflagration.

chloride of sodium; the whole is mixed well, and the mixture heated gradually during eight or ten minutes to low redness in a wrought-iron spoon. When cold, it is treated 5 or 6 times with *hot* water, and the solution transferred to a filter by means of a pipette. Finally, the residue is boiled with water, and thoroughly washed on the filter with *boiling* water. The filtrate and washings are now tested for their alkalinity according to § 219 or § 220.

The calculation of the amount of sulphur in pyrites depends on the following considerations: To neutralise the quantity of carbonate of soda originally added, a certain amount of a standard acid would have been necessary, and to neutralise the liquid extracted by hot water from the fused mass a smaller quantity would naturally be required, smaller indeed in the same proportion as the amount of the sulphur oxidised to sulphuric acid is greater. The acid, therefore, corresponding with the quantity of carbonate of soda employed, *minus* the acid actually used for neutralizing the extract from the fusion, represents the quantity of sulphur in the pyrites, reckoning 1 equiv. of sulphur for 1 equiv. of acid. 1000 c.c. of the standard acid prepared according to § 219, corresponds with 30·19 grams of sulphur, 1000 c.c. of normal acid (prepared according to § 215) corresponds with 16 grams of sulphur.

Finally, as a check, a portion of the insoluble residue left on treating the fused mass with water, is tested for sulphur by treating it with hydrochloric acid, &c.

The process takes 30 or 40 minutes, and yields results differing—according to PELOUZE—not more than 1 to 1·5 per cent. from the truth. Any loss of carbonate of soda causes the sulphur to be too high.

In applying the method to spent pyrites, salt is not added; 5 grams of the roasted ore, 5 grams of pure anhydrous carbonate of soda, and 5 grams of chlorate of potassa are taken.

In this process the sulphur present in the form of sulphate is estimated as if it were combined with metals.

The fact that this method, which is still used in not a few works, yields results which are not sufficiently trustworthy, has been demonstrated by BARRESWIL, BOTTOMLEY, BOCHEROFF, LUNGE, and with particular thoroughness by KOLB,* the latter having minutely elucidated the causes of the want of exactness. The circumstance that in this process chlorine is evolved, that sulphuric acid can be evolved from any ferric sulphate which has been formed and not yet decomposed again, as also that chloride of sulphur may be evolved, and that the fused mass sometimes contains sulphide of sodium, easily allows of the alkalimetric titre of the fused mass appearing too high and the amount of sulphur too low—whilst, on the other hand, arsenic, which is converted into arsenate of soda, and silicic acid, which at the high temperature employed, gives rise to the formation of insoluble double silicates containing soda, make the sulphur come out too high.

These errors which become proportionately greater, the smaller the amount of sulphur in the pyrites or burnt pyrites, may be avoided (or at all events to a very great extent) if the following process is adopted.

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* Journ. de Pharm. et de Chim. (iv.) 10, 401; Zeitschr. f. anal. Chem. 9, 407.

b. J. KOLB'S* *Method.*

1 gram of pyrites or 5 to 10 grams of burnt pyrites in a finely divided state is mixed with 50 grams of similarly prepared cupric oxide and 5 grams of carbonate of soda, and the mixture heated. The conversion of the sulphur into sulphate of soda takes place. according to KOLB, without fusion or disturbance of the mass, and at a sufficiently low temperature, so that there is no fear of decomposing the refractory sulphates or of any action of the silicic acid on the carbonate of soda.

The calculation is effected in the same way as in PELOUZE's method. It must be pointed out that in this process the arsenic is estimated as its equivalent of sulphur, and that the easily decomposable sulphates such as gypsum, introduce the same error as in PELOUZE's method.

15. URANIUM COMPOUNDS.

§ 257.

The following process, described by A. PATERA† is to be recommended for quickly estimating the amount of uranium in uranium ores. The weighed quantity of the ore to be tested is dissolved in nitric acid, avoiding as far as possible any excess of acid; the acid solution is then diluted with water, at once supersaturated with carbonate of soda, and heated to boiling to completely dissolve the uranic oxide and decompose any bicarbonate of lime, ferrous oxide, &c., produced; the precipitate is collected and washed with hot water. The filtrate which, except uranium, contains only traces of foreign metals, is precipitated with caustic soda, and the orange-coloured precipitate of acid uranate of sodium washed slightly only and dried. The dried precipitate is separated from the filter, heated to redness in a platinum crucible and the ash of the separately incinerated filter added to it. The contents of the crucible are transferred to a small filter, washed, dried and heated to redness. It consists of $NaO,2Ur_2O_3$, 100 parts of which, according to PATERA, are equivalent to 88·3 parts of uranosouranic oxide, Ur_3O_4. The method yields results so satisfactory that it is employed in Joachimsthal as the recognised test in the purchase of uranium ores.

CL. WINKLER‡ who has frequently had occasion to test the method, says of it that it yields results which are correct, agreeing so nearly with those obtained by other methods of analysis, that it is undoubtedly, for technical purposes at least, sufficiently accurate. With ores rich in copper, WINKLER obtained results which were rather too high. A small amount of copper, always passes into the alkaline solution under these circumstances and is thrown down along with the uranate of soda on the subsequent addition of caustic soda.

16. SILVER COMPOUNDS.

§ 258.

The silver compounds which are most frequently the subject of examination in chemical laboratories are either ores containing silver, or silver alloys.

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* Journ. de Pharm. et de Chim. (iv.) 10, 401; Zeitschr. f. anal. Chem. 9, 407.

† Dingler's Polytechn. Journ. 180, 242; Zeitschr. f. anal. Chem. 5, 228.

‡ Zeitschr. f. anal. Chem. 8, 387.

A. Silver Ores.

Silver ores can be analysed both by wet and dry methods. If it is only a question of determining the amount of silver present, especially in the case of small quantities of silver, the dry methods usually attain this object most rapidly and accurately, but if all the constituents have to be estimated the wet method must under all circumstances be chosen. An exact qualitative analysis must first be made, and the individual metals separated by the methods in the fifth section of the first part. If on treating the ore with nitric acid it yields a solution containing all the silver, it must first be treated in this way; in other cases, especially in the analysis of ores containing arsenic and antimony (antimonial silver, brittle silver ore, ruby silver ore, miargyrite, polybasite, Fahl ore, &c.), it is preferable to heat the powdered ore in a current of chlorine and first separate the non-volatile metallic chlorides from the volatile, see Vol. I. p. 470 (where also the apparatus to be used is depicted and described), Vol. I. p. 480, 8 and § 261.

The examination of silver ores in the dry way is best and most accurately carried out by roasting the ore along with pure lead, whereby the elements which accompany the silver ore are either volatilised as oxides and acids or run into a slag with the lead oxide. When oxidation has proceeded far enough, the process is stopped, and the unoxidised lead containing all the silver is separated from the slag and driven off in a cupel. The details of the process are given in § 259 (Estimation of Silver in Galena).

B. Silver Alloys.

Of the silver alloys, those of silver and copper have by far the most frequently to be examined. That these also can be treated either by the dry or the wet method follows from Vol. I. p. 234, *ff*, and p. 472, 11. This is again referred to with the object of adding Volhard's volumetric method,* Vol. I. pp. 234–241, which is distinguished by its simplicity and accuracy as well as by the circumstance—in contradistinction to Gay-Lussac's method—that it does not presuppose an approximate knowledge of the amount of silver in the alloy. This was not yet known at the time the author was engaged on that particular section of the first volume.

This method rests on the precipitation of the silver as sulphocyanate from a nitric acid solution, the moment when the sulphocyanate of ammonium or potassium used as the precipitant begins to be present in excess, being ascertained by the sulphocyanate of iron reaction.

For the preparation of the titrating solution, Volhard uses sulphocyanate of ammonium, others, B. Lindemann,† for instance, prefer sulphocyanate of potassa. Both salts are equally stable in dilute solution. The presence of a minute amount of chlorine in the sulphocyanate is not prejudicial in the estimation of silver but any considerable quantity is very injurious and Volhard's reason for preferring sulphocyanate of ammonium is that it is more easily procured free from chlorine than sulphocyanate of potassium is.‡

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* Journ. f. prakt. Chem. (N.F.) 9, 217; Ann. d. Chem. u. Pharm. 190, 1; Zeitschr. f. anal. Chem. 13, 171; 17, 482.

† Zeitschr. f. anal. Chem., 16, 352.

‡ Sulphocyanate of ammonium is prepared from substances which are usually

7·5 to 8 grams (approximately weighed) of sulphocyanate of ammonium is dissolved in water, made up to 1 litre, and standardised by means of a solution of silver of known strength. For this purpose, exactly 10 grams of chemically pure silver is weighed out, dissolved in 160–200 c.c. of pure nitric acid of sp. gr. 1·2, and the nitrous acid completely driven off by long heating, after the silver is entirely dissolved. When cold, it is diluted to 1 litre, and 50 c.c. containing 0·5 gram of silver, is taken out in a pipette, diluted with about 150 c.c. of water, and 5 c.c. of a cold saturated solution of iron ammonia alum added. If the colour of the ferric salt is apparent, a little more nitric acid is added, until the colour of the iron salt disappears. The sulphocyanate of ammonium solution is now run in from a burette. At first, only a white precipitate is formed which remains suspended in the liquid, and imparts to it a milky appearance, but on adding more sulphocyanate of ammonium each drop produces a blood red cloud which quickly disappears on shaking. When the point of complete precipitation of the silver is approached, the sulphocyanate of silver collects in flocks and the liquid commences to clear, without however becoming completely so as long as there is still any trace of silver left in solution. As soon as all the silver is thrown down, the flocculent precipitate subsides. The addition of the sulphocyanate solution is continued—finally by drops—until the liquid has become clear and has assumed a light brown tint, as pale as possible, but permanent after frequent shakings. This coloration is best observed if the liquid is held, not against the light, but away from the window and against a white wall. The test is repeated and—if the results are identical—the sulphocyanate of ammonium solution is diluted on the basis of the results obtained, so that 50 c.c. is equivalent to exactly 50 c.c. of the silver solution, or 1 c.c. of sulphocyanate of ammonium solution to 0·010 grams of silver.

For the estimation of silver in alloys, the same process is adopted as that just prescribed for standardising the sulphocyanate of ammonium solution. If exactly 1 gram of alloy be taken then every $\frac{1}{10}$ c.c. of sulphocyanate solution indicates 1 per thousand of silver.

In using this method, the following points must be observed :

1. Nitrous acid must not be present either in the solution or in the nitric acid which is subsequently added. Should the nitric acid contain nitrous acid, the latter must be removed by boiling, and the purified acid kept excluded from bright light.

2. The action of the sulphocyanate solution must be carried on in the cold as, if warm, the sulphocyanic acid is decomposed by nitric acid, and the colour of the ferric sulphocyanate is destroyed.

3. The solution of iron ammonia alum must always be used in great excess and in approximately the same relation to the total amount of the liquid.

4. It makes no difference in the result whether the amount of free nitric acid present is greater or less.

5. The presence of copper does not affect the result provided, it does not exceed 70 per cent. of the alloy. When an alloy is richer in copper than this limit, a suitable amount of pure silver is weighed out and

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quite, or nearly, free from chlorine. It contains, as a rule, no chlorine compounds or only minute quantities, from which it can be easily freed by a single recrystallisation from boiling water. Commercial sulphocyanate of potassium always contains more chlorine than the ammonium salt (VOLHARD, *loc. cit.*).

added to the sample, care being taken that the amount of copper in the sample weighed (1 gram) does not exceed 0·7 gram.

6. Mercury must not be present in the solution. Should an alloy contain mercury this must be first driven off by heating to redness.

7. Palladium makes the titration of the silver inexact, as it is shown as silver.

8. In the presence of nickel or cobalt, the recognition of the final reaction requires practice; otherwise it is easy to add a few drops too much of the sulphocyanate solution. By titrating back carefully with silver solution, the pure colour of the nickel or cobalt solution appears so suddenly and so sharply that it is easy to observe the end point in titrating back, when the colour of the solution has become yellowish brown through the admixture of the ferric sulphocyanate.

17. Lead Compounds.

§ 259.

A. Galena.

Galena, the most widely distributed and important of the lead ores, contains, in addition to lead and sulphur, frequently or occasionally, smaller or larger quantities of zinc, copper, antimony, arsenic, iron, silver, traces of gold, and usually more or less gangue insoluble in acids.

In the following paragraphs are described 1. The estimation of all the constituents of the Galena; 2. The determination of the Lead alone; 3. The estimation of the Silver in galena in the dry way; and 4, in the wet way.

1. Determination of all the Constituents of Galena.

a. A weighed quantity (1 to 2 grams) is oxidized with highly concentrated red fuming nitric acid, free from chlorine and sulphuric acid (see Vol. I. p. 387 *a*). For this purpose, a capacious flask is used, which should be covered with a watch-glass during the operation; but the tube in which the powder was weighed must not be put into the flask. If the acid is sufficiently strong, the sulphur will be fully oxidized. After it has been warmed gently for a long time, the contents of the flask are washed into a porcelain dish, 3 to 4 c.c. of pure concentrated sulphuric acid, previously diluted with a little water, is added, and the mixture heated on a water-bath until all the nitric acid has evaporated. It is then diluted with 50 to 60 c.c. of water, filtered, the residue washed with water containing sulphuric acid, and the latter displaced by alcohol. The alcoholic washings are collected separately.

α. When the *residue* is dry, it is ignited and weighed (Vol. I. p. 244, 3); it consists of sulphate of lead, gangue which is not decomposed by the acid, silicic acid, &c. The whole, or an aliquot part, of the residue is heated to boiling with hydrochloric acid, and filtered after some time, but so that the precipitate does not come on the filter; a fresh portion of hydrochloric acid is poured on the residue, boiled with it again, allowed to subside, &c., and the operation repeated until the sulphate of lead is completely dissolved; finally the residue is brought on to the filter, and washed with boiling water until every trace of chloride of lead is removed; the *residue* is then dried, heated to redness, and weighed. On subtracting the weight found from that of the original residue, the difference expresses the quantity of *sulphate of lead* which the latter contained. Instead of using hydrochloric acid, the sulphate of lead may also be dissolved by heating with an aqueous solution of tartrate or acetate of ammonia to which some ammonia has been added, or acetate of soda may be used; or it may be first converted into carbonate of lead by digestion with solution of carbonate of soda, then washed, and dissolved in dilute nitric acid. One of the methods just mentioned must be employed for separating the sulphate of lead from the gangue, if there is any fear that the latter will be attacked by hydrochloric acid.

β. The *sulphuric acid solution* is free from any weighable trace of lead if the process has been properly conducted, but it contains the metals which were present in the ore along with the lead. Some hydrochloric acid is first added to test for *silver;* if a turbidity or precipitate is produced, the liquid is kept for some time in a warm place until the chloride of silver has subsided. This is filtered off, and may be determined according to Vol. I. p. 232. In the case of very small quantities, it is preferable to incinerate the filter along with the precipitate in a porcelain crucible, ignite the residue for a short time in hydrogen, dissolve the trace of metallic silver in nitric acid, evaporate the solution in the crucible to dryness, and then take up the residue with water, and estimate the silver in the solution by PISANI's method (Vol. I. p. 240). As a rule, however, the galena contains so little silver that an accurate determination in 1 or 2 grams of the ore is not possible; for a silver determination, a larger quantity must therefore be treated according to § 259, 3 or 4.

The clear liquid, or that which has been filtered from the chloride of silver, is precipitated with sulphuretted hydrogen. The precipitate generally contains a little *sulphide of copper* and *sulphide of antimony*, occasionally also other *sulphides*. These are separated, as well as the metals in the filtrate which are are precipitable by sulphide of ammonium (*iron*, *zinc*, &c.), according to the methods of Section V. of the first Part. With respect to the separation of antimony from arsenic comp. this vol. pp. 352, 353.

b. For the estimation of the *sulphur*, a fresh portion of the finely pulverized ore is treated exactly as directed in Vol. I. p. 383, 1, *a*. As there pointed out, the treatment of the solution of the fused mass with carbonic acid before filtering must not be omitted. If a wet method is preferred, thə author recommends that given in Vol. I. p. 388, *b*.

2. Estimation of Lead alone, in Galena.

The method for analysing lead salts described by F. STOLBA*, namely, separation of the lead by means of zinc in the wet way, is also recommended by STORER † and MASCAZZINI ‡ for the estimation of lead in galena. Both weigh the separated lead as such, the former after drying in a current of coal gas, the latter after fusion with a reducing flux. The one brings the galena powder, hydrochloric acid and zinc directly together, the latter first converts the galena into sulphate of lead by heating it to redness with sulphate of ammonia before acting on it with zinc and hydrochloric acid. It appears that these methods are not to be recommended, at least G. C. WITTSTEIN and A. B. CLARK, junr.,[*] in testing STORER's method, obtained very unsatisfactory results, and F. MOHR in his investigations also found that the results were unsatisfactory on weighing the separated lead either after drying or after fusion with reducing fluxes.

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* Journ. f. prakt. Chem. 101, 150; Zeitschr. f. anal. Chem. 7, 102.

† Chem. News, vol. xxi. p. 137; Zeitschr. f. anal. Chem. 9, 514.

‡ Zeitschr. f. anal. Chem. 10, 491.

However, F. MOHR[†] based the following process for estimating lead in galena, on the decomposition of the latter by zinc. About 2 grams of the finely powdered ore is weighed and placed in a small porcelain dish or pan, and ordinary hydrochloric acid (of 1·12 sp. gr.) added, the dish or pan being covered with a convex glass, and heated, finally to boiling. Sulphuretted hydrogen is evolved and lead chloride separates. When the acid ceases to act, from the unattacked galena becoming surrounded by chloride of lead, and the hydrochloric acid is saturated with the latter, a small ball of zinc is introduced. A brisk evolution of hydrogen occurs, and lead is deposited on the zinc. On gently warming, fresh portions of lead chloride are continually dissolved and decomposed, until finally the evolution of sulphuretted hydrogen ceases, and the liquid appears quite clear and colourless. It is then poured off and the lead thoroughly washed with water,[‡] which is easily accomplished by simple decantation. The separated lead is dissolved in dilute nitric acid, the solution filtered off from the undissolved gangue, evaporated with sulphuric acid, and the estimation of the lead proceeded with as in Vol. I. p. 244 *a*. *β*.

3. Estimation of the Silver in Galena, and Testing for Gold (in the Dry Way).

As mentioned above, the method described in § 259,1, does not suffice to detect and estimate the very small quantities of silver,[§] and the trifling traces of gold which, according to PERCY and SMITH,[||] are often found in galena. To effect this, it is, in the first place, usually necessary to obtain a button containing the whole or part of the lead of the galena along with the whole of the silver and gold, and then to treat this regulus in the wet or dry way.

PREPARATION OF THE BUTTON.

a. Methods suitable for poor Argentiferous Galenas.

a. 20 grams of the finely pulverized galena is mixed with 60 grams of anhydrous carbonate of soda and 6 grams of nitrate of potassa, the mixture put into a Hessian crucible, covered with a layer, 8 mm. deep, of decrepitated chloride of sodium, and fused, finally at a bright red heat, so as to produce a fusible slag. The crucible after being allowed to cool slowly, is broken to pieces, and the button, which must be clean and compact, is flattened on an anvil, and freed from all adherent impurities by boiling with water. By this process, according to BERTHIER (and the author), 75—78 per cent. of lead is obtained from pure galena, instead of the 86·6 per cent., which it actually contains, but the whole of the silver is found in the button. To understand the process, it must be borne in mind that on fusing galena with carbonate of soda, out of contact with the air, metallic lead is produced, along with a slag consisting of a double sulphide of lead and sodium, and sulphate of soda.

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[*] Zeitschr. f. anal. Chem. 11, 460.

[†] *Ibid.* 12, 143.

[‡] According to STOLBA (Zeitschr. f. anal. Chem. 7, 103), distilled water is unsuitable for washing the spongy lead as, even when previously boiled and cooled without access of air, it dissolves some lead. He recommends, therefore, the employment of spring water for the washing.

[§] Argentiferous galenas generally contain only between 0·03 to 0·18, rarely above 0·5 per cent. silver; and a great many contain far less than the minimum mentioned.

[||] Phil. Mag. 7, 126; Journ. f. prakt. Chem. 61, 435.

$$4(NaO,CO_2) + 7PbS = 4Pb + 3(PbS,NaS) + NaO,SO_3 + 4CO_2.$$

The nitrate of potassa serves to decompose the sulpho-salt, whereby the lead is liberated, and the sodium and the sulphur oxidized.

β. 20 grams of pulverized galena is mixed with 40 grams of black flux (prepared by deflagrating 1 part of nitrate of potassa with 2½ parts of acid tartrate of potassa) and 5—6 grams of very small iron nails, and the mixture fused in a Hessian crucible, at a bright red heat. If a refractory gangue is present, 2 to 3 grams of glass of borax should be added. The galena is first decomposed by the carbonate of potassa and the carbon, with separation of lead and formation of a double sulphide of lead and potassium, which is then desulphurized by the iron at a higher temperature, the lead separating in a state of fusion. When the crucible is cold, it is broken to pieces, and the button treated as in *a*. Care must be taken that the lead encloses no nails. According to BERTHIER, this process gives 72—79 per cent. of lead; from pure galena, however, 85·5 per cent. may be obtained if the temperature is not too high.*

b. Method more particularly suitable for rich Argentiferous Galenas (Scorification).†

This process requires scorifiers of baked fire-clay (fig. 106), and a properly constructed muffle furnace, with good draught.‡

4 grams of the finely pulverized ore is mixed with 16 grams of lead free from silver (which may be prepared in the laboratory, most conveniently by precipitating solution of acetate of lead with zinc), in a scorifier, and the mixture covered uniformly with 16 grams more of the lead. According to the nature of the impurities contained in the ore, certain fluxes have to be added, namely, borax, quartz, or glass. Borax is added when the ore contains much lime, magnesia, zinc, &c., the quantity varying with the amount of the extraneous bases in the ore, and may occasionally be as much as 2·5 grams. If the ore contains quartz or silicates, no borax is added, or only a little, not more than 0·5 gram, whilst to ores which contain little or no silicic acid, either free or in combination, a very small quantity of glass or quartz is added.

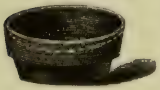
FIG. 106.

The above proportions of ore and lead may be considered the normal quantities; but if the former contains a considerable amount of zinc blende or pyrites, 48 or 64 grams of lead are used, and in the presence of compounds of copper or tin even more.

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* "Metallurgische Probirkunst," by KERL, Leipzig, 1866, p. 155.

† Comp. BODEMANN and KERL's excellent "Anleitung zur Probirkunst," edited by KERL, 2nd edit. Clausthal, 1857, p. 287. Also "Metallurgische Probirkunst," by KERL, Leipzig, A. Felix, 1866, p. 241; "Probirkunst," by C. A. M. BALLING, Braunschweig, Vieweg & Sohn, 1879, p. 299.

‡ For a detailed description of such a furnace, consult the above-named works.

The scorifiers, properly charged, are introduced into the muffle (see fig. 110), previously heated to bright redness, and the mouth of the latter is closed with live coals, to accelerate the fusion of the lead. The lead melts, whilst the lighter ore floats on the surface and is roasted, the fumes evolved during the roasting differing according to the nature of the escaping products; sulphur forms light grey, zinc dense white, arsenic greyish-white, and antimony bluish, fumes.

After 15 to 20 minutes, a fluid slag forms, which completely surrounds the fused metal at the edges, dense fumes of lead rising at the same time from the surface of the latter. Refractory samples require a good 35 minutes before this point is attained and the fused metal presents a smooth surface.

The coals are now removed from the mouth of the muffle, the damper of the furnace closed, and the lead oxidized by the current of air until the scoriæ entirely or nearly cover the metal; the heat is then once more raised to a high temperature for about 5 minutes, so as to render the slag very fluid. The process of scorification generally occupies half an hour, but never more than an hour.

The scorifiers are now taken out of the muffle with tongs about 3 feet long, of the form shown in fig. 107, and the metal and slag poured into a suitable mould, consisting of an iron or copper plate in which there are hemispherical cavities or cups of 3 to 6 cm. in diameter. The plate should be warmed, and the cavities rubbed over with reddle or chalk.

The alloy obtained must form a single button, separating readily from the slag. The button is hammered out so that it may be readily laid hold of with the 3 ft. tongs shown in fig. 108, and subsequently placed on the cupel without projecting over the edge.

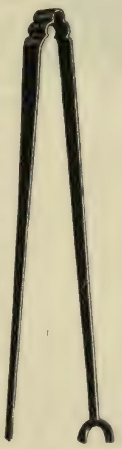
FIG. 107.

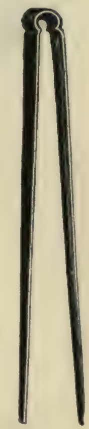
FIG. 108.

In the process here described, the ore is first roasted, and litharge produced, which then decomposes the metallic sulphides, the sulphur being oxidized to sulphurous acid, and the metals separated the oxide of lead formed also dissolves the earths and other oxides and removes them as slag.

DETERMINATION OF THE SILVER IN THE ARGENTIFEROUS LEAD BUTTON.

The determination of the silver may be effected either in the wet or in the dry way. In chemical laboratories, the want of proper muffle furnaces generally compels the selection of the former (see § 259, 4, *a*); whereas in metallurgical laboratories the dry way (cupellation) is invariably employed.*

For this operation, small cups of compressed bone-ash, called *cupels*, fig. 109, are required. Although 1 part by weight of the porous mass of the cupel can absorb the oxide from 2 parts by weight of lead, yet, as a rule, it is reckoned as taking up the oxide of 1 part of lead only; the weight of the button should, therefore, not greatly exceed that of the cupel.

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* The description of this interesting and important operation is taken from BODEMANN and KERL'S work already mentioned.

FIG. 109.

When the muffle (see fig. 110) is sufficiently heated to show half the bottom at a white heat, it is ready to be charged; the empty cupels are introduced, and gradually pushed back until they are at a bright red heat; for it is necessary that the alloy of lead and silver now to be introduced should melt quickly, as otherwise small particles of lead are apt to stick to the upper edge of the cupel. If the furnace is very hot, the separation of the silver from the lead soon begins; if not, pieces of red-hot charcoal are placed at the mouth of the muffle, to accelerate the process. As soon as the surface of the lead is in motion, the damper of the furnace is closed, and only a small piece of charcoal is left at the mouth of the muffle. The great point now is to effect the complete separation of the silver from the lead at the lowest possible temperature, for if it be raised too high, some of the silver will be absorbed by the cupel along with the litharge; on the other hand, too low a temperature must be avoided, or else the assay will become chilled, and even though the temperature should afterwards be raised sufficiently high, the results are not satisfactory.

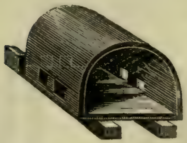

FIG. 110.

If the cupellation is properly conducted, the lead fumes rising from the cupels slowly curl up to the middle of the muffle, and a ring of small imperfect crystals of oxide of lead forms at the edge of the cupel, which is at a reddish-brown heat. If the lead fumes disappear immediately above the cupels, whilst the latter are at a bright red heat, and no crystals are formed at the edges, the heat is too strong. If, on the other hand, the fumes ascend to the vault of the muffle, and the edges of the cupels look dark brown, the temperature is too low, and there is danger of the button solidifying.

Towards the end of the cupellation, the temperature must be again raised, as the bead becomes less fusible as the proportion of silver in it increases, and the last portions of lead require a higher temperature for their conversion into litharge and absorption by the cupel. Care must be taken, however, not to raise the heat too soon or too suddenly, and never to such a temperature as to remelt the ring of flake litharge. As the process draws to a close, only a thin net-like film of litharge remains on the silver, iridescence makes its appearance on the surface, and then the globule of silver suddenly becomes visible in its purity; the assay *flashes*. It is now allowed to cool very slowly, in order to avoid *spitting* of the metal, which the violent escape of the oxygen absorbed by the molten silver would otherwise occasion.

The upper surface of the bead must be silvery white and brilliant, and hemispherical or round, and easily detached from the cupel by means of pincers, whilst the lower surface, after brushing, must be clean and silvery white, although not lustrous. Beads with projecting ridges or knobs on the lower surface, arising from fissures or depressions in the cupel, must be rejected, as the projecting parts always contain lead. The beads, after being properly cleaned, are weighed. If the lead added was not absolutely free from silver, a correction must be made, the amount of silver in this lead having been previously determined.

The silver bead, after weighing, may be tested for gold, and the latter, if possible, determined as directed in Vol. I. p. 476 (**169**).

There is invariably a small loss of silver in cupellation. Burbidge Hambly's experiments* have shown that this loss increases with the proportion of the lead to the silver; in an assay made with 1 part of silver to 1 of lead, the loss of silver was 5·5 in 1000 parts of silver; with 1 part of silver to 15 parts of lead, 16·2; and with 1 part of silver to 35 of lead, 18·8.

4. Estimation of the Silver in Galena in the wet way.

a. A lead regulus containing the whole of the silver is prepared according to § 259, 3 *a*, *α*. or *β*., and, after being purified as far as possible, is dissolved in moderately dilute nitric acid free from chlorine; the solution is then largely diluted, and decomposed with a little very dilute hydrochloric acid or a solution of lead chloride. The turbid liquid is left in a warm place until all the chloride of silver has subsided, and then the latter is collected on a filter, washed as thoroughly as possible with boiling water, and estimated finally as metallic silver (this vol. p. 364, *β*). The author found that this method gave satisfactory results when the quantity of silver was not too small (Analytical supplement 91), but it cannot be used in the case of extremely small amounts, because very slight traces of chloride of silver remain dissolved in a liquid containing much plumbic nitrate (Hampe †). For the concentration of silver in lead see this vol. p. 373, 14.

b. The nitric acid solution of the regulus is treated by Pisani's method, Vol. I. p. 240. Care must be taken to have the sulphuric acid, employed in precipitating the lead, and the carbonate of lime used to neutralise the acid, perfectly free from chlorine compounds. The author has had no experience of this method.

c. C. A. M. Balling ‡ recommends the following method in which the preparation of a regulus is dispensed with. 2 to 5 grams of the finely powdered galena is placed in a relatively large porcelain crucible, with 3 to 4 times its weight of a mixture of equal parts of carbonate of soda and nitrate of potassa, covered up, and heated until the contents are fused, stirring it well with a heated glass rod. When cold, the crucible is placed in a porcelain dish, the fused mass softened with water, and the contents of the crucible emptied into the dish; after being warmed, filtered, and washed, it is replaced in the dish, and the lead oxide containing the silver is dissolved in dilute pure nitric acid. It is then evaporated to dryness, the residue extracted with water to which a little nitric acid has been added, warmed, the solution filtered into a flask, the filter washed with hot water, and the whole allowed to cool. Iron ammonia alum solution is then added to the filtrate, and the silver titrated by Volhard's method with sulphocyanate of ammonium solution (see this vol. p. 361). The sulphocyanate of ammonium solution should be so diluted that 1 c.c. is equivalent to 1 c.c. of a silver solution containing 1 gram of silver per litre. 1 c.c. of the sulphocyanate of ammonium solution is thus equivalent to 1 milligram of silver. The author, as yet, has no personal experience of this method.

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* Chem. Gazette, 1856, p. 185. Chem. Centralblatt, 1857, p. 509.

† Zeitschr. f. anal. Chem. 11, 221.

‡ Chem. Centralblatt, 1879, p. 490.

B. Varieties of Metallic Lead.

The metallic lead which has to be examined differs greatly in purity. The analysis of refined lead (soft lead), crude lead, and hard lead is described in the following sections.

a. Analysis of Refined Lead (Soft Lead).

This contains 99·96 to 99·99 per cent. of metallic lead, together with extremely minute quantities of other metals, namely, silver, copper, bismuth, cadmium, antimony, arsenic, iron, nickel, cobalt, zinc, and manganese.

*First Method.**

1. The lead to be analysed is cut up into large pieces, and the surfaces of each scraped with a bright knife until thoroughly clean and bright. They are then warmed with dilute hydrochloric acid, washed with hot water, and dried quickly. If this cleansing be omitted, it is to be feared that the accuracy of the result may be appreciably affected by adhering impurities.

2. Exactly 200 grams of the pieces of lead, cleansed as in 1, are weighed out and dissolved, in a capacious flask of 1 to 1½ litres capacity, in pure dilute nitric acid, of which about 500 c.c. of sp. gr. 1·2 are required, adding sufficient water (about 500 c.c.) to prevent any nitrate of lead from separating out. Dissolution is assisted by suitable warming, unnecessary excess of nitric acid being avoided, and the solution is allowed to stand for 12 to 24 hours.

As 200 grams of lead yield 310 grams of lead nitrate, and 1 part of the latter requires about 2 parts of water for its solution, if the solution is made up to about 1 litre, no lead nitrate can crystallise out. If this occurs, however, it results from using a large excess of nitric acid, as it is well known that nitrate of lead is much less soluble in dilute nitric acid than in water.

3. As a rule (that is, in the case of all pure soft leads), the solution is clear, and remains so. It is only in the case of leads which are rather richer in antimony that a more or less decided white precipitate forms either at once or on standing. These less usual cases are treated of under 15; in this place it is pre-supposed that the solution has remained clear.

4. The solution is completely transferred to a 2 litre measuring flask, 115 grams (about 62 to 63 c.c.) of absolutely pure concentrated sulphuric acid—approximately weighed or measured—is added, and the mixture allowed to cool; it is then filled up to the mark, agitated as thoroughly as possible, and allowed to stand. The sulphuric acid added is calculated in such proportion as to give an excess of about 10 to 12 grams of hydrated sulphuric acid. After the precipitated sulphate of lead has entirely settled down, the clear or almost clear liquid is drawn off by means of a syphon previously filled with a small quantity of the

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* R. FRESENIUS, on the analysis of soft or refined lead. (Zeitschr. f. anal. Chem. 8, 148).

same liquid; in this way more than 1750 c.c. can be drawn off. Of course this may also be effected by filtering through a dry filter, but the first method is preferable as excluding all impurities. Of the clear or almost clear liquid, 1750 c.c. is accurately measured, and evaporated under a perfectly clean draught cupboard, without covering the dish with paper, until vapours of sulphuric acid come off freely, a sign that the nitric acid is driven off. It is then allowed to cool, about 60 c.c. of water added, the small quantity of sulphate of lead thrown down is collected on a small filter which has been thoroughly extracted with hydrochloric acid and water, and the precipitate is washed with water.

5. The slight precipitate of sulphate of lead thus obtained frequently contains small portions of the acids of antimony. It is dissolved in hydrochloric acid, diluted with at least 10 times as much sulphuretted hydrogen water as the hydrochloric acid employed for solution, warmed, and treated with sulphuretted hydrogen gas. After settling, the precipitate is collected on a filter, washed, the filter spread out in a basin and the precipitate heated for a short time, nearly at the boiling heat, with a solution of pure sulphide of potassium or ammonium, with the addition of a small quantity of pure sulphur. It is filtered, washed, and the filtrate acidified with hydrochloric acid, the precipitate formed being allowed to settle down at a gentle heat.

6. Into the sulphuric acid solution obtained in 4, diluted, if necessary, to about 200 c.c. with water, sulphuretted hydrogen is passed until the precipitate settles down, the temperature being kept at about 70°; it is then allowed to remain 12 hours in a moderately warm place, filtered through a small filter, and the precipitate washed. The filtrate and washings are treated as in 9, but the small precipitate is heated with sulphide of potassium solution and a trace of sulphur, as in 5. The filtrate containing sulphide of potassium is acidified with hydrochloric acid, and the precipitate formed is left to subside at a gentle heat.

7. The small precipitate left undissolved by the sulphide of potassium, and containing the metals of the fifth group is treated—after spreading out the filter in a small basin—with dilute nitric acid (about 1 part of nitric acid of sp. gr. 1·2 to 2 parts of water) almost at the boiling temperature. When the precipitate has dissolved, the solution is filtered, and the filter washed, dried, and incinerated. The nitric acid solution into which the filter ash has been put, is evaporated with the addition of 2 c.c. of dilute sulphuric acid until the nitric acid is removed; a little water is now added, the trace of sulphate of lead which will have separated is filtered off, and the filtrate is almost neutralised with pure caustic potash; carbonate of soda is added, then some cyanide of potassium free from sulphide of potassium, and the mixture heated gently. If a precipitate is formed, it is dissolved in dilute nitric acid after being washed, and the bismuth estimated in the solution by precipitating it with carbonate of ammonia and weighing as oxide. To the solution filtered from the bismuth precipitate, or which has remained clear after the addition of cyanide of potassium, some more cyanide of potassium is added, and then a few drops of sulphide of potassium. If a precipitate is formed, it may contain the sulphides of cadmium and silver; this is collected, dissolved in hot dilute nitric acid, any silver present is precipitated by a few drops of hydrochloric acid, the filtrate evaporated almost to dryness and tested to see if cadmium is precipitated on the

addition of carbonate of soda. This cadmium is finally estimated as oxide; the best way being to dissolve the well washed precipitate in nitric acid, evaporate, heat to redness and weigh the residue. To the liquid filtered from the sulphides of cadmium and silver, or which has remained clear after the addition of sulphide of potassium, a little sulphuric and nitric acids are added, as well as a few drops of hydrochloric acid, and the whole evaporated until there is no longer any odour of hydrocyanic acid; the clear, or, if necessary, filtered solution is precipitated with sulphuretted hydrogen, and the copper estimated as sulphide (Vol. I. p. 257). When the quantity is small, the estimation should be controlled by a volumetric analysis, by re-dissolving the sulphide of copper in nitric acid, evaporating the solution to dryness with sulphuric acid, and decomposing the sulphate of copper by iodide of potassium (Vol. I. p. 258, *a.*).

When no cadmium is present, the separation of bismuth from copper by ammonia and carbonate of ammonia is simpler, but if the former is present, which cannot be known as a rule, the analysis is thereby made more difficult since part of the cadmium may come down in the bismuth precipitate and part remain in the solution with the copper. It should never be forgotten that the acid copper solution must be tested for silver by means of hydrochloric acid, previous to the final precipitation with sulphuretted hydrogen, as otherwise the sulphide of copper may be contaminated with sulphide of silver.

8. The precipitates obtained in 5 and 6 by acidifying the sulphide of potassium solution with hydrochloric acid are collected on a small filter, dissolved in excess of caustic potash while still moist, treated with chlorine, and the antimony and arsenic separated and estimated by Bunsen's method (see this vol. pp. 352–353). The sulphide of antimony can be advantageously collected in an asbestos filter tube, treated as in Vol. I. p. 273, and weighed as black trisulphide of antimony.

9. The filtrate obtained in 6, together with the washings if they exceed 500 c.c., can be concentrated, made just alkaline with ammonia, and sulphide of ammonium added; the flask, filled up to the neck, is then corked and allowed to remain for at least 24 hours. In any case it is not filtered until the slight precipitate has completely subsided. The filtrate is just acidified with acetic acid, acetate of ammonia added, and the whole evaporated at a gentle heat, so that, if there is any slight trace of sulphide of nickel still held in solution by the sulphide of ammonium, it may be thrown down along with the sulphur. After subsidence, this sulphur is collected on a filter.

10. The precipitate produced by sulphide of ammonium in 9, and filtered off, is treated on the filter, and directly after it has been collected, with a mixture of about 6 parts of sulphuretted hydrogen water and 1 part of hydrochloric acid of sp. gr. 1·12, the liquid which passes through being repeatedly poured back. In this way, the iron and zinc sulphides become dissolved whilst the sulphides of nickel and cobalt remain behind. This filter and that obtained in 9, which may contain nickel in the sulphur, are incinerated together, treated with some aqua regia, and evaporated to a small bulk, the solution is then made just alkaline with ammonia, some carbonate of ammonia added, the whole filtered, and the ammoniacal filtrate heated in a platinum basin with an excess of pure caustic potash, until no more ammonia is evolved. Should weighable flocks separate, they are collected, dried, incinerated, heated to redness, weighed, and

tested before the blowpipe to see if the oxide of nickel contains oxide of cobalt.

11. The filtrate obtained in 10, by treating the sulphide of ammonium precipitate with very dilute hydrochloric acid, is concentrated by evaporation, finally with the addition of a little nitric acid, and precipitated with ammonia; the flocks of hydrated ferric oxide are collected after warming, dissolved again in hydrochloric acid, reprecipitated with ammonia, washed, thoroughly dried, incinerated, and weighed as ferric oxide. As a control, it can be fused with a little acid sulphate of potassa, reduced with zinc, and the ferrous oxide estimated volumetrically by permanganate of potassa.

12. The filtrate from the ferric oxide is mixed with a little sulphide of ammonium and allowed to remain in a warm place for at least 24 hours. If weighable flocks separate, these are collected, washed, and treated at once on the filter with dilute acetic acid to extract any sulphide of manganese that may be mixed with them. If any traces of sulphide of zinc remain on the filter, they are best weighed after being converted into zinc oxide by VOLHARD's method (see this vol. p. 277). The acetic acid solution, however, is evaporated to a small bulk and tested with caustic potash for any manganese that may be present.

13. In calculating the constituents estimated thus far, it should not be forgotten that the amounts obtained correspond not with 200 but with 179 grams of lead. These figures result from the consideration that the 2-litre flask filled up to the mark contains 45 c.c. of sulphate of lead and 1955 c.c. of solution, and that only 1750 c.c. of this has been used; hence 1955 c.c.: 200 grams : : 1750 c.c.: 179·03, or in round numbers 179 grams.

14. The estimation of the silver* is best carried out by cupellation (this vol. pp. 367 and 368) because very slight traces of silver cannot be precipitated by hydrochloric acid from the nitric acid solutions of lead (see this vol. p. 369, 4, *a*). As many soft leads, for example the Oberharz refined lead (HAMPE), contain only 0·0005 per cent of silver, 200 grams of the lead must be got rid of to obtain 1 milligram of silver. An experimenter lacking accommodation for the cupellation of such large quantities of lead can, acccording to MERRICK† reduce the mass by fusing it in a fairly roomy Hessian crucible, and adding half its weight of nitrate of potassa. The heat is then increased until the crucible is white hot up to the rim; the contents are stirred with a pointed iron rod, the crucible removed from the fire before it is eaten through by the lead oxide, allowed to cool, and broken up. In this manner, the silver may be concentrated so that its estimation by the wet process is rendered possible.

15. Lastly, the case of leads containing rather more antimony must be considered. With these, a white precipitate of antimony oxide and antimoniate of oxide of antimony is formed on standing, or even during solution; this may, moreover, also contain arsenic, and traces of other metals. The precipitate is collected, washed, dissolved in hydrochloric acid,

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* The cause of the difference in the estimation of silver in lead bars is often to be found in the unequal distribution of the silver in the bars. This metal collects to a greater extent in the portions which solidify first, than in those which remain liquid longer; the outside and upper portions therefore are richer than the inner and lower. SCHWEITZER (Zeitschr. f. anal. Chem. 16, 504) found from this cause, in a bar of lead, a difference between 79·83 oz. (middle portion) and 104·54 oz. (upper length) per ton of lead.

† Zeitschr. f. anal. Chem. 10, 494.

diluted to 100 c.c. precisely, with water containing tartaric acid, and of this a quantity in the proportion 1955 : 1750 (see above, 13.), that is to say, 89·5 c.c., is taken and precipitated with sulphuretted hydrogen; the precipitate formed being treated along with that mentioned in 6 as produced by sulphuretted hydrogen.

16. If other metals besides those noticed in the foregoing paragraphs are found in soft leads, the process will of course require to be correspondingly modified.

17. The amount of lead is found by difference. There is no object in making a direct determination of the lead, as it would not in any way control the accuracy of the estimation of the foreign metals.

Second Method. W. Hampe's.*

1. The carefully cleaned metal is beaten out on a polished steel anvil into thin sheets by a polished steel hammer, and cut up into small strips with scissors. In estimating the foreign metals, other than silver, which are contained in lead, 400 grams are used. Quantities of 200 grams each are dissolved in two large, covered glass beakers in a mixture of 500 c.c. of nitric acid of 1·2 sp. gr., with 500 c.c. of water; 70 c.c. of pure concentrated sulphuric acid (previously diluted with a little water) is then added to the still hot, clear solution in order to precipitate the lead. The mixture is now allowed to cool, and as much as possible of the clear liquid is poured out of both beakers into a porcelain basin, the united precipitates being washed, either 8 to 10 times with water containing sulphuric acid, by decantation, or on a vacuum filter the platinum cone of which is fitted with a very small filter. The washings are concentrated by boiling, added to the decanted liquid, and finally the whole is evaporated and heated until the greater part of the sulphuric acid is driven off.

2. The residue obtained in 1 is mixed with water when cold; this will cause the separation of more sulphate of lead. The strongly acid liquid is now boiled for some time so that no basic bismuthic sulphate may remain with the lead sulphate, a few drops of hydrochloric acid are added to throw down the silver, and the precipitate is collected, and washed with dilute sulphuric acid.

3. The precipitate obtained in 2, and containing a little antimoniate of lead, is boiled with sulphide of potassium solution and filtered. This solution is called A.

4. The solution in 2, filtered off from the sulphate of lead and chloride of silver, is treated as in the first method (6. and 7.), to throw down the metals of the fifth and sixth groups. In this way, a solution containing the metals of the fourth group is obtained, and also a precipitate. On treating the latter with sulphide of potassium solution, however, an insoluble residue is obtained, and a solution (B) containing the remainder of the antimony and arsenic.

5. The solutions A and B obtained in 3 and 4 are treated with dilute sulphuric acid to throw down the metallic sulphides, the sulphuretted hydrogen is driven off by evaporation, and the precipitate collected and washed with water to which a little ammonium nitrate and a few drops of nitric acid have been added (as antimony sulphide, if washed with pure water passes easily through the filter as a turbidity). After

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* Zeitschr. f. das Berg-, Hütten-, und Salinenwesen in dem preussischen Staate, 18, 195; Zeitschr. f. anal. Chem. 11, 215.

any excess of sulphur has, if necessary, been removed from the precipitate by carbon bisulphide, it is dissolved in strong freshly prepared sulphide of ammonium, the solution evaporated on the water-bath, the residue treated with hydrochloric acid and chlorate of potassa at a moderate heat, and the arsenic and antimony separated as in Vol. I. p. 488 (**204**). The sulphide of antimony which is thrown down by passing sulphuretted hydrogen into the filtrate from the arsenate of ammonia and magnesia, is dissolved, after washing, in warm, freshly prepared sulphide of ammonium; the solution is then evaporated in a weighed porcelain crucible, at first at a very gentle heat on the water-bath, and the residue left on evaporation is oxidised by fuming nitric acid, heated to redness, and the antimoniate of oxide of antimony thus obtained is weighed.

6. The separation of the metals of the fifth group, the sulphides of which constitute the residue insoluble in sulphide of potassium obtained in 4, is carried out as in the first method (7.), although HAMPE prefers dissolving the carbonates of bismuth and cadmium in hot nitric acid, evaporating the solution in a weighed platinum crucible, heating the residue to redness, and weighing the oxides thus obtained.

7. From the filtrate obtained in 4, the metals of the fourth group are precipitated by sulphide of ammonium after evaporation and addition of ammonia to alkaline reaction. If the solution is brown from dissolved nickel sulphide, it is boiled until the brown colour disappears; it is then filtered, washed first with water and then with alcohol, any sulphur present removed by extraction with carbon bisulphide, and the nickel, cobalt, iron, manganese, and zinc separated as in the first method (9. to 12.) Finally the cobalt and nickel are separated by means of nitrite of potassa.

8. The silver is estimated by cupellation.

b. Analysis of Crude Lead and Hard Lead.

Crude lead contains from 95 to 99 per cent. of lead—0·01 to 0·18 of silver, and somewhat larger amounts of the other metals which have been taken into consideration in the analysis of soft lead. Hard lead differs from the other varieties of lead, chiefly in containing a relatively large amount of antimony, which varies somewhere between 2 and 6 per cent. For the analysis of crude lead, 50 to 200 grams are taken according to the degree of purity; whilst for hard lead 5 to 10 grams are sufficient. Both varieties are treated with a warm mixture of equal parts of nitric acid of sp. gr. 1·2 and water, until all the soluble matter is dissolved; it is then diluted with water, allowed to settle, and filtered off from the white precipitate which always remains, consisting mainly of oxygen compounds of antimony, and antimoniate of oxide of lead. After washing the precipitate, it is removed from the filter without destroying the latter, either by careful washing, or by drying and rubbing; in the former case the water containing the precipitate is evaporated in a porcelain crucible, and the precipitate fused with 3 to 4 parts of liver of sulphur, the crucible being covered. The fused mass is dissolved in hot water and filtered through the filter first used; this is then treated along with the precipitate thrown down from the sulpho-salt solution on adding dilute sulphuric acid to it, also the precipitate insoluble in liver of sulphur solution and consisting, according to HAMPE, of sulphides of lead, of silver, and of bismuth, together with the analogous precipitate to be obtained from the sulphuric acid solution.

Lead is thrown down from the nitric acid solution by adding to it a moderate excess of sulphuric acid, the precipitate is allowed to subside, the solution poured off, and the precipitate washed by decantation, or on a vacuum filter (see p. 374, Second Method, 1.); the filtrate is then evaporated until the greater part of the excess of sulphuric acid is driven off. According to HAMPE, the residue left on evaporation is best treated as follows. A little water and hydrochloric acid are added, it is boiled, allowed to cool, and alcohol is added; it is then filtered after 12 hours, and washed with alcohol containing hydrochloric acid. In this way all the arsenic, antimony, copper, bismuth, cadmium, iron, &c., are obtained in solution together with small amounts of lead. The alcohol is allowed to evaporate, the solution precipitated with sulphuretted hydrogen, the metals of the fifth and sixth groups separated by fusion with sulphide of potassium, and the individual metals estimated by the methods prescribed for soft lead. If it is desired to use BUNSEN'S method for separating antimony from arsenic, it is advisable, as the amount of antimony is relatively large, to dissolve the sulphide of antimony first precipitated in caustic potash and to repeat the separation so as to obtain the sulphide of antimony quite free from arsenic. The estimation of iron, zinc, and silver is carried out as in *a.* of this section.

C. Oxides and Salts of Lead.

The oxides and salts of lead met with in commerce, such as massicot, litharge, white lead, and sulphate of lead, present no difficulties in analysis. The analysis of minium and the impure varieties of sugar of lead, however, requires a brief mention.

a. Minium.

Minium is frequently the subject of analysis in technical laboratories, and it is by no means a question of merely detecting impurities and adulterations, but rather of especially determining the relation between the peroxide of lead and the oxide of lead. The impurities insoluble in acid remain behind when the minium is dissolved in dilute nitric acid with the addition of a little spirit of wine, sugar or oxalic acid. By making the nitric acid solution up to a known volume, one portion can be employed in testing qualitatively for the presence of dissolved foreign metals, and the other for the quantitative estimation of the lead according to Vol. I. p. 244, 3. The determination of any carbonic acid possibly present may be carried out according to Vol. I. p. 340, taking a larger quantity of minium, and using nitric acid to drive off the carbonic acid. The amount of peroxide of lead can be determined in the same way as peroxide of manganese in manganese ores, and especially by means of oxalic acid and sulphuric acid as described in this vol. pp. 291 and 294, as well as iodimetrically according to this vol. p. 296 *b.*

Finally, F. LUX* prescribes the following process for quickly determining the value of minium, and, for practical purposes, with sufficient accuracy. This is also based on the action of oxalic acid on peroxide of lead, according to the equation $PbO_2 + 2(C_2O_3,HO) = PbO,C_2O_3 + 2CO_2 + 2HO$ (in which oxalic acid is considered as a monobasic acid). If the original amount of oxalic acid added be known, and a determination is made of the portion remaining undecomposed after all action has ceased, which is easily effected by a solution of permanganate of potassa after dissolving the oxalate of lead in nitric acid, the difference gives the amount of oxalic acid decomposed. From this, the amount of peroxide of lead can be calculated, since 1 equiv. of C_2O_3 corresponds with 1 equiv. of peroxide of lead. It is convenient to employ N/5 oxalic acid solution, containing 12·6 grams of crystallised oxalic acid per litre, and an equivalent solution of permanganate of potassa, 1 c.c. of which corresponds with 1 c.c. of the oxalic solution (Vol. I. pp. 217–218); 2·07 grams of the minium to be tested (the fiftieth part of the lead equivalent expressed in grams) is treated with 20 to 30 c.c. of dilute nitric acid (of sp. gr. 1·2) in a 300 c.c. porcelain basin, warmed gently, and stirred. After a few minutes, the minium is decomposed into oxide, which dissolves, and peroxide, which remains undissolved; 50 c.c. of the oxalic acid solution is now added, and the whole heated to boiling. The peroxide of lead is immediately decomposed and dissolved, whilst the insoluble impurities (barytes, sulphate of lead, clay, sand, ferric oxide, or any large amount of gypsum) are left. Without removing the insoluble residue, the liquid is kept boiling, and 5 to 10 c.c. of the permanganate of potassa solution is straightway added; as soon as this is decolorised, fresh portions are added until all the oxalic acid in the solution is decomposed. The titration is considered to be ended when the rose coloration produced by 2 drops of permanganate of potassa does not completely disappear in ½ minute. (If the permanganate of potassa solution is added only drop by drop from the first, the decomposition of the oxalic acid goes on very slowly.) The number of c.c. of permanganate of potassa solution used is deducted from 50; the difference gives the percentage amount of peroxide of lead present.

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* Zeitschr. f. anal. Chem. 19, 153.

After the liquid has been decolorised by a drop of oxalic acid solution, it is almost neutralised by ammonia, a sufficient quantity of acetate of ammonia or acetate of soda is added, and the lead estimated volumetrically by chromate of potassa according to the method given in Vol. I. p. 247, *b*. By deducting from the total lead the amount present as peroxide, the amount of oxide in the minium is ascertained. The determination of the peroxide is not interfered with by any of the impurities or adulterations present in minium; the amount of lead, however, can only be accurately determined in the manner described provided carbonate of baryta is absent (this, however, should hardly ever be found in minium).

b. Sugar of Lead.

In addition to the crystallised, almost pure, sugar of lead, whose properties and composition may be mostly decided without quantitative analysis, other varieties of sugar of lead occur in commerce in respect of which this cannot be said, and which contain, sometimes more, sometimes less oxide of lead and acetic acid according to the mode of preparation. To these belong the so-called amorphous white sugar of lead, as well as the yellow and brown sugars of lead (which are prepared by dissolving litharge in impure acetic acid made from wood vinegar, that is in rectified or in crude pyroligneous acid).

All the varieties of sugar of lead can now be simply analysed by a process devised by the author,* by a suitable combination of gravimetric with volumetric analysis. The principle of the method is as follows:

The lead acetate to be tested is dissolved in water in a measuring flask, and normal sulphuric acid is added in slight excess; the whole of the oxide of lead is thus obtained as sulphate of lead in the precipitate, whilst the whole of the acetic acid, together with the slight excess of sulphuric acid, remains in the solution. If the flask is filled up to the mark, and then as much water is added as corresponds with the volume of the lead sulphate formed (which, as the amount of lead oxide in lead acetate only varies between ascertained limits, can be determined with sufficient accuracy), the above-named acids are obtained in a known volume of liquid. If the excess of sulphuric acid is now determined in a measured quantity of the clear liquid by means of chloride of barium, the amount of lead can be easily calculated; for, as the total amount of sulphuric acid is known, and the quantity remaining in the solution has been determined, the difference gives the amount in combination with the lead oxide, and hence —by calculating 1 equiv. of lead oxide for each equivalent of this sulphuric acid—the amount of the oxide can be ascertained.

In an equally simple manner the amount of acetic acid (together with the small quantities of propionic acid, butyric acid, &c.) can be estimated, for, if the number of c.c. of normal soda solution be ascertained, which is required to neutralise a measured quantity of the liquid containing the acetic acid, &c., along with the excess of sulphuric acid, and the amount of the same necessary for the neutralisation of the already known excess of sulphuric acid be deducted, the difference will correspond with the acetic acid, &c., and the amount of the latter can easily be calculated.

In practice, the following simple process is recommended:

A half-litre flask is required which has a mark not only at 500 c.c. but also at 501·3 c.c. 10 grams of the acetate of lead to be examined is weighed out and dissolved in water in the 500 c.c. flask; 60 c.c. of normal sulphuric acid is then added, the flask filled up to the 501·3 c.c. mark, closed with a caoutchouc stopper, shaken well and allowed to settle.

1. The sulphuric acid in 100 c.c. of the clear solution is determined by means of chloride of barium, the volume calculated to 500 c.c., the result subtracted from 2·4 grams of sulphuric acid (the contents of the 60 c.c. of normal sulphuric acid), and the amount of oxide of lead equivalent to it calculated from the difference. As this refers to 10 grams, the percentage is obtained by multiplying the result by 10).

2. Another 100 c.c. of the clear solution is taken, a few drops of litmus tincture added to it, and then normal soda until neutral; the number of c.c. used is calculated to 500 c.c., and from this is subtracted the number of c.c. corresponding with the sulphuric acid (found in 1.) as contained in the 500 c.c. solution; from the difference, the acetic acid contained in the 10 grams of acetate of lead can be calculated.

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* Zeitschr. f. anal. Chem. 13, 30.

18. MERCURY COMPOUNDS.

§ 260.

A. Ores of Mercury.

The analysis of ores of mercury hardly requires special mention, everything requisite being given in §§ 118, 162, 163 and 164. As a rule, the process described in § 118, 1. *a*, for the estimation of mercury effects this object in the best and safest manner. Mention may, however, be made here of A. ESCHKA'S* method of estimating mercury in its ores, which can be carried out comparatively quickly, and gives results which are sufficiently accurate for technical purposes, especially in testing poor ores.

A porcelain crucible is required, with an even rim, ground if necessary, on which a highly concave, bevel-edged lid of gold plate fits tightly. The powdered ore is placed in the crucible, about 5 grams being taken if the ore contains 1–10 %; 2 grams if 10–30 %; and 1 gram if over 30 % of mercery. The powdered ore is mixed with about half its weight of *clean* iron filings quite free from oil, by the aid of a glass rod, and the mixture is covered with an uniform layer of iron filings, 0·5 to 1·0 cm. deep; the gold cover is weighed and placed on the crucible, the concavity of the gold cover being filled with distilled water to keep it cool, and the crucible is heated for 10 minutes, the point of the flame playing round the bottom of it. Heating for this length of time suffices to drive the whole of the mercury out of the ore and on to the gold lid. The cover is now taken off, the water poured away, and the mercurial mirror on the convex side is rinsed with alcohol, dried at 100°, and weighed after it has become quite cold in a desiccator. The increase in weight of the lid corresponds with the weight of mercury contained in the ore examined. In weighing the gold cover, it is placed on a porcelain crucible as a support, this being weighed each time along with it.

When the test is ended, the cover is heated in a good draught cupboard, at first very gently, and afterwards to a bright red heat, so as to remove the mercury and make it ready for the next assay. If the necessary care is taken in heating it, the gold cover alters but very little in weight after repeated use.

If larger quantities of mercury are volatilised during the examination, a thin fluid amalgam is formed, which flows about when the lid is inclined; in this case the alcohol used for rinsing must, of course, be collected in order not to lose any of the mercury.

From ESCHKA'S experiments it appears that the results obtained by this process are always somewhat too low. The loss amounted, for instance, to 0·002 gram of mercury in 0·083 gram of cinnabar, and to 0·005 gram of mercury in 0·2855 gram of cinnabar.

B. Metallic Mercury.

The analysis of commercial mercury is attended with certain difficulties, owing to the large quantity that must be taken in order to find and estimate the foreign metals, the quantity of which is frequently very small. According to the author's experience,* the object can very well be attained in the following way:

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* Oesterr. Zeitschr. f. Berg- und Hüttenwesen, 1872, No. 9; Dingler's polyt. Journ. 204, 47; Zeitschr. f. anal. Chem. 11, 344.

1. 100 grams of the mercury to be examined is dissolved in an excess of pure moderately strong nitric acid, in a glass flask, and heated to gentle boiling for some time, so as to completely convert the mercurous salt first formed into a mercuric salt. If an insoluble residue remains, this is collected, and after washing and drying, fused with a little liver of sulphur; the fused mass is treated with water, filtered off from any sulphide of lead, and the solution acidified with hydrochloric acid.

After subsidence, it is filtered through an asbestos filter tube, washed, dried, and heated in a current of chlorine (Vol. I. p. 485, **196**). The metallic chlorides obtained in the receiver are precipitated with sulphuretted hydrogen, reserving the precipitate in the meanwhile; the contents of the asbestos filter-tube, however, are treated with aqua regia and the solution tested for gold (Vol. I. p. 269, 6. β.).

2. The acid solution of mercuric nitrate is evaporated to dryness in a porcelain basin with the addition of 56 grams of pure concentrated sulphuric acid, which has been previously diluted with 120 grams of water, the heating being continued until all the nitric acid is driven off; the residue is then diluted with water, and the whole rinsed into a stoppered flask holding 3 to 4 litres. The mercury is now in the flask, partly in solution as mercuric sulphate, partly undissolved as basic sulphate; along with these, all the foreign metals are present as sulphates, either dissolved or undissolved.

3. Ammonia is added to the contents of the flask until alkaline, then so much sulphide of ammonium that the latter largely predominates, and the whole is digested for 24 hours at a gentle heat, shaking frequently. The liquid above the dense black precipitate should be yellow and smell strongly of sulphide of ammonium; if this is not the case, some more yellow sulphide of ammonium must be added and the digestion prolonged. The sulphide of ammonium solution containing the metals of the sixth group (antimony, tin, arsenic, &c.) is filtered through a large smooth filter, and the dense, black precipitate of mercuric sulphide is washed with water to which a little sulphide of ammonium has been added.

4. The liquid containing sulphide of ammonium is acidified with hydrochloric acid, the precipitate (reserved from 1.) which was obtained from the solution of the metallic chlorides volatilised in the current of chlorine is added to it, and the whole allowed to stand for 2 to 3 days; the supernatant liquid is syphoned off and the precipitate, which consists mostly of sulphur, is collected on a filter. After it has been washed with water and then with alcohol, it is treated with bisulphide of carbon. The residue left is treated again with warm sulphide of ammonium, to remove as far as possible traces of mercury and copper, and the tin, antimony, and arsenic, when present, are estimated in the filtrate by one of the methods mentioned in § 165. For a convenient method of separating arsenic and antimony, refer also to this vol. p. 352, *b*.

5. If the presence of alkalis or alkaline earths in the mercury is

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* Zeitschr. f. anal. Chem. 2, 343.

suspected, the liquid obtained in 4, and separated from precipitated sulphur and the metallic sulphides of the sixth group, is tested for them.

6. The precipitate of mercuric sulphide, &c., obtained in 3, together with any traces of the sulphides of lead, copper, and mercury, obtained in 1 and 4, is rinsed into a flask; and if a large quantity of water has been used for this purpose, the precipitate is allowed to subside, the supernatant liquid filtered off through a small filter, and the small quantity collected on it is again rinsed into the main precipitate. 50 c.c. of pure nitric acid of sp. gr. 1·2 and about 1 gram of nitrate of ammonia are added to the 500 c.c. or so of liquid in the flask, and the whole boiled gently for an hour. The liquid is allowed to clear, and the nitric acid solution filtered and evaporated to a small bulk; it is then diluted, and any silver present is precipitated by a few drops of dilute hydrochloric acid. The clear liquid, or the filtrate from any chloride of silver which may have been deposited after long standing, is evaporated with the addition of excess of pure sulphuric acid until all the nitric acid is driven off; it is then diluted, heated, the precipitated sulphate of lead is collected and washed, first with water containing sulphuric acid and then with alcohol, and the lead estimated as in Vol. I. p. 244, *a.* *β*. The liquid filtered off from the sulphate of lead is precipitated by sulphuretted hydrogen after the addition of a little hydrochloric acid, and the bismuth, copper and cadmium, if these are all present, are estimated in the precipitate as prescribed in this vol. p. 371, 7.

7. To the liquid filtered from the precipitate produced by sulphuretted hydrogen in 6, ammonia, chloride of ammonium and sulphide of ammonium are added in a flask, which must be almost filled with the liquid; it is allowed to remain for 24 hours, and in the precipitate which is then deposited, the metals of the fourth group, zinc particularly, are estimated. The iron which is found here can only be considered as originating in the mercury if the reagents and the filter were absolutely free from iron.

8. Lastly, a sample of the mercuric sulphide exhausted by boiling dilute nitric acid and dried, is finally heated to redness in a porcelain crucible in a good draught cupboard. If the manipulation has been properly conducted, no residue should be left.

9. If mercury when shaken with dilute hydrochloric acid yields a solution containing mercuric chloride, the mercury contains mercuric oxide. The quantity of this is obtained from the amount of mercury in the hydrochloric acid solution.

19. COPPER COMPOUNDS.

A. Copper Ores.

§ 261.

Of the copper ores, those containing metallic copper, cuprous oxide, cupric oxide, or copper salts, require no particular consideration, but detailed accounts of the complicated analysis of the sulphuretted copper ores (copper pyrites, purple copper ore, copperglance, &c.) as well as of those containing large amounts of antimony and arsenic (Fahlerz, or grey copper ore, &c.) are necessary.

1. Methods for Complete Analysis.

a. Sulphuretted Copper Ores.

The sulphuretted copper ores, of which copper pyrites is the most frequently subjected to analysis, always or almost always contain copper, iron, sulphur and gangue. Whether other metals (nickel, cobalt, zinc, manganese, arsenic, antimony, silver, &c.) are also present must be ascertained by a qualitative analysis.

The very finely pulverised mineral is dried at 100°.

1. The amount of sulphur in it is best determined by the methods prescribed for pyrites (this vol. pp. 351, 1., and 356, 1.).

2. For the estimation of the *copper*, *iron*, and *gangue*, about 1 gram is treated with concentrated nitric acid in an inclined, long necked flask, strong hydrochloric acid is added after a short time, and the whole digested until completely decomposed; it is then evaporated almost to dryness at a gentle heat. If the hydrochloric acid used has not been sufficient to remove all the nitric acid, more hydrochloric acid must be added and the evaporation repeated as prescribed. Hydrochloric acid is now added to the residue, the mixture warmed, diluted with water, and the undissolved *gangue* dried, heated to a redness, and weighed.

If the ore is mixed with galena, the residue may include sulphate of lead; this must be removed, before the drying and ignition, by digesting it with acetate or tartrate of ammonia.

The hydrochloric acid solution is diluted, precipitated hot by sulphuretted hydrogen, filtered after standing for a time, and the sulphide of copper washed with water containing sulphuretted hydrogen; the filter is then spread out in a basin, warmed with sulphide of sodium solution, diluted, filtered, and washed. The sulphide of copper is now dissolved in aqua regia, diluted and filtered, and the washed filter incinerated, the ash also is treated with a little aqua regia, and the solutions containing the copper strongly concentrated; ammonia is added until the free acid is neutralised, then carbonate of ammonia, and the mixture, after being allowed to stand a considerable time at a gentle heat, is filtered, acidified with hydrochloric acid, precipitated hot by sulphuretted hydrogen, and the *copper* in the precipitate estimated according to Vol. I. p. 257, 3. *a.*

The liquid filtered from the still impure sulphide of copper first precipitated by sulphuretted hydrogen, is concentrated, oxidised with nitric acid, and the *iron* thrown down as in Vol. I. p. 437 (**82**) and estimated in the hydrochloric acid solution of the precipitate either according to Vol. I. 435, 2, or volumetrically as in Vol. I. p. 225, *a.*

3. For estimating the constituents present in small amount, about 10 grams of the finely powdered ore is treated with fuming nitric acid, and in order to remove the nitric acid, evaporated with a slight excess of sulphuric acid until vapours of the latter begin to come off. It is then allowed to cool, water is added, the mixture heated, filtered into a weighed flask holding about 1 litre, and the residue washed with water containing sulphuric acid. Any *lead* present remains in the residue as sulphate of lead; this is extracted by a hot solution of acetate of ammonia mixed with a little ammonia, and the lead in the solution estimated by precipitation with sulphuretted hydrogen and conversion of the sulphide of lead into sulphate. The residue left after the exhaustion by acetate of ammonia is heated with hydrochloric acid, diluted, filtered into the

sulphuric acid solution first obtained, and, whether clear, or turbid through the separation of a small amount of argentic chloride, is precipitated hot with sulphuretted hydrogen; water is then added until the flask is nearly full, mixed thoroughly, allowed to subside during a long time, and the whole weighed. The weight of the empty flask and of the sulphide of copper from 2 being known, the difference is the weight of the solution in the flask. As much as will come away clear is syphoned off, and the flask and residue are re-weighed. The liquid, whose weight is now known, is filtered if not already perfectly clear, and an aliquot part of the solution thus obtained is boiled with the addition of nitric acid, and precipitated by ammonia added in excess; the precipitate after a slight washing is dissolved in hydrochloric acid, and the iron precipitated as basic salt according to Vol. I. p. 437 (**82**); the filtrate is tested by adding some ammonia, to see if it gives a precipitate of hydrate of alumina, and the liquid filtered off from the alumina precipitate, if such is formed, is acidified with acetic acid, and the *nickel*, *cobalt*, *zinc*, and *manganese* estimated if present, in the manner described in this vol. p. 310, 8. *Alumina* is estimated in the precipitates obtained by means of carbonate of ammonia and, if necessary, ammonia, by the method given in Vol. I. p. 436, (**78**). As the weight of the alumina, nickel, cobalt &c. obtained are from a portion only of the solution, it must not be forgotten to calculate them to the total solution.

To the residue containing sulphide of copper, which remains in the weighed flask, caustic soda or potash is added to alkaline reaction, then sulphide of potassium or sodium, and the mixture warmed for a long time. It is then diluted with water until the flask is almost full, mixed, allowed to cool, and weighed. By deducting from this weight, that of the flask, of the sulphide of copper and of the sulphide of iron here present, the weight of the alkaline solution containing the metals of the sixth group is ascertained. By means of a syphon as much of the solution is removed as can be drawn off clear, the weight of this is ascertained by weighing the flask with the residue, and the solution, filtered if necessary, is precipitated with hydrochloric acid; the precipitate after being allowed to subside, is washed, digested with hydrochloric acid containing bromine, filtered, and the excess of bromine removed from the filtrate by the careful addition of sulphurous acid. It is then precipitated at 70° with sulphuretted hydrogen, the *arsenic* and *antimony* being separated and estimated according to this vol. pp. 352 and 353, and the values calculated from the part to the whole. If the ore contains any *mercury* this would pass, as mercuric sulphide, into the solution containing sulphide of potassium, or sulphide of sodium, and would be obtained along with the sulphide of antimony and sulphide of arsenic; it must be separated from these by sulphide of ammonium.

4. Should any other metals of the fifth group be present in addition to copper, lead and mercury, the sulphide of copper must ultimately be washed, dissolved in nitric acid and the solution used for the estimation of the other metals of the fifth group. See § 263. Any silver present is however best determined by cupellation (this vol. pp. 366 and 367).

5. With regard to testing for Thallium see this vol. p. 355, 6.

b. Ores containing Arsenic and Antimony (Fahlerz).

In analysing grey copper ore, the estimation of copper, silver, mercury, iron, zinc, antimony, arsenic, lead, sulphur, and gangue must be kept in view, although many of these ores do not contain all the metals mentioned. The analysis is best commenced by heating about 1 gram of the finely powdered ore in a slow current of chlorine.* For this purpose, the apparatus figured in Vol. I. p. 470 is used, modified in one point only, in that the bulb tube D is replaced by a similar one with two bulbs. The powdered ore is introduced into the bulb attached to the apparatus for generating chlorine, and as soon as the air has been almost entirely driven out of the generating flask and the drying apparatus, the bulb tube, which is slightly inclined downwards, is connected with C. The tubes E and F contain a solution of tartaric acid to which some hydrochloric acid has been added. The decomposition of the ore begins at once, the bulb becomes heated, and the volatile chlorides are carried forward, partly as far as the empty second bulb of the bulb tube, and partly to E and F. When the bulb containing the ore has become almost cold, it is heated very gently by a small flame while a slow current of chlorine is passed through it so as to drive the volatile chlorides into the second bulb. It is not advisable to continue the heating until all the ferric chloride has passed into the second bulb, but rather to stop as soon as vapour of ferric chloride alone comes off. After the piece of tube between the two bulbs has become clean, and the apparatus is cold, the tube between the two bulbs is cut in two by means of a file mark and a piece of ignited charcoal, and the portion attached to the bulb containing the sublimate is closed by a short glass tube fused together at one end, and moistened internally. After allowing the apparatus to remain for 24 hours for the sublimate to absorb moisture and so admit of its solution in water without heating, the contents of the bulb are treated with a solution of tartaric acid mixed with hydrochloric acid. If the liquid becomes turbid from the separation of oxygen compounds of antimony, it is warmed until they dissolve; if sulphur has separated, the liquid must be filtered.

The analysis now consists of the examination of the residue left in the first bulb, of the volatile chlorides in the solution, and lastly in the separate estimation of the sulphur.

1. The *residue* contains or may contain chlorides of silver, lead, and copper, a portion of the ferric chloride, and the whole or nearly the whole of the chloride of zinc and the gangue. It is digested with dilute hydrochloric acid for some time, diluted copiously with water, allowed to stand for a considerable time, and the chloride of silver filtered off and washed with boiling water until all the chloride of lead is removed; the chloride of silver is then separated, if necessary, from the *gangue* by ammonia, the chloride of silver is re-precipitated by nitric acid from the ammoniacal solution, and the *silver* therein estimated according to Vol. I. p. 234. The filtrate is precipitated with sulphuretted hydrogen (Vol. I. p. 457), and then the *copper* and *lead* in the precipitate are separated according to Vol. I. p. 465, 2. The filtrate is however kept meanwhile.

2. The *solution* which contains the mercury, antimony, arsenic, and

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* Compare H. Rose, Handbuch der analyt. Chem. 6th edition by R. Finkener, vol. ii. p. 479; F. Wöhler, Die Mineralanalyse in Beispielen, 2nd edition, p. 73.

a part of the iron, as well as zinc, and possibly also some lead, is precipitated at 70° by sulphuretted hydrogen, filtered, and washed. In the precipitate, the sulphide of mercury is separated from the sulphides of antimony and arsenic by means of sulphide of ammonium (Vol. I. p. 474, 2) and the *mercury* determined as sulphide (Vol. I. p. 251, 3); *antimony* and *arsenic*, however, are best separated by BUNSEN's method (this vol. pp. 352 and 353). The sulphide of mercury thus obtained is boiled with dilute nitric acid, and any small quantity of *lead* present is estimated in the filtrate.

The liquid filtered off from the precipitate produced by sulphuretted hydrogen is united with the similar solution obtained from the residue in 1., and the *iron* and *zinc* therein estimated (this vol. p. 354), as also any alkaline earths that may be present.

3. The proportion of *sulphur* is best determined by fusing a fresh sample with carbonate of soda and nitrate of potassa as in the case of iron pyrites (this vol. p. 356, 1).

II. ESTIMATION OF THE AMOUNT OF COPPER IN COPPER ORES.

1. By ordinary Gravimetric Analysis.

The process is conducted exactly as in § 261 1 *a*, weighing the copper as sulphide of copper, and omitting the estimation of the other metals, &c.

2. Estimation of the Copper by Electrolysis.

If it is a question of daily estimating copper a number of ores of a similar kind, the electrolytic method is preferable to all others.

This was first described by WOLCOTT GIBBS[*] and by LUCKOW,[†] and brought into general use by the Mansfeld "Ober-Berg- und Hutten-direction," in Eisleben, for ores containing neither antimony, arsenic, nor bismuth.[‡] The method is unsuitable, however, for ores containing these metals as they are deposited on the copper and blacken it.

Some further references to the subject of the electrolytic determination of copper are given in the footnote.[§]

a. Production of the current.

The Mansfeld Department of Mines at first made use in their laboratory of MEIDINGER's element for the production of the current, later of PINKUS' modified MEIDINGER, and afterwards employed the thermopile, of MURE and CLAMOND,[||] as improved by CLAMOND.[¶] HERPIN also, who worked with the BUNSEN battery, a small GRAMME machine, and the CLAMOND thermopile, recommends the use of the latter by preference. For chemical laboratory work, Clamond's pile is undoubtedly the most convenient apparatus for the production of a suitable current. The reader is, therefore, referred to the report of the Mansfeld Ober-Berg- und Huttendirection* for particulars of the Meidinger-Pinkus element and its working, the Clamond thermopile alone being described here.† This apparatus is depicted in Figs. 111, 112, and 113.

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[*] Zeitschr. f. anal. Chem. 3, 334.

[†] Dingler's polyt. Journ. vol. 177, p. 296; Zeitschr. f. anal. Chem. 19, 1.

[‡] Zeitschr. f. anal. Chem. 8, 23; 11, 1, and 14, 350.

[§] MERRICK (Americ. Chem. 2, 136), WRIGHTSON (Zeitschr. f. anal. Chem. 15, 299), HERPIN (*ibid.* 15, 335), OHL (*ibid.* 18, 523), A. CLASSEN and M. A. v. REIS (Ber. deutsch. chem. Gesell. 1881, p. 1627), A. RICHE (Zeitschr. f. anal. Chem. 17, 216, and 21, 116).

[||] Dingler's polyt. Journ. 207, 125.

[¶] *Ibid.* 215, 427. Zeitschr. f. anal. Chem. 14, 350.

Fig. 111 is a perspective view, Fig. 112 a vertical section, also showing the armature, and Fig. 113 a cross section of the bars and their armatures in position.

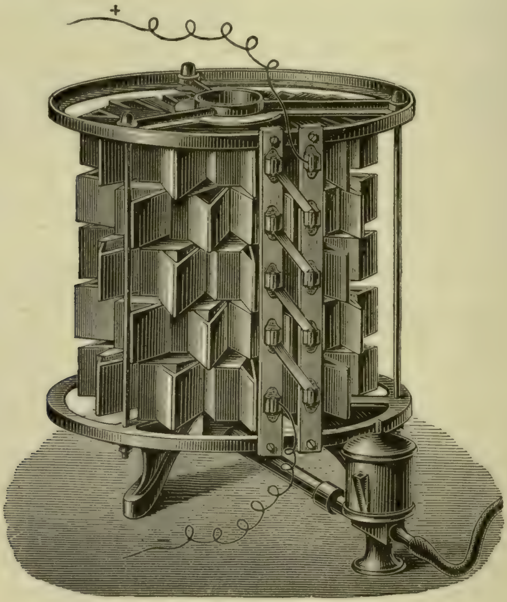

Fig. 111.

The elements are composed of iron, and an alloy of zinc with antimony. In order to impart greater durability to the latter, the bars should be cast in moulds heated to a temperature slightly below the fusing point of the alloy, which, moreover, should not be strongly over-heated. The elements are arranged radially round a centre as shown in Fig. 113, several such rings superimposed forming the pile.

In Fig. 113, the bars of zinc antimony alloy are those marked *B*, whilst *L* denotes the tinned iron plate; as these iron plates serve as leads from one element to the other, they are laid on the upper surface of the bars *B*; as the latter expand more than the iron, the contact increases on heating. The individual elements are insulated by layers of asbestos (*see r* in Fig. 112), as are also the different superimposed rings of elements *B*. The whole forms a cylinder on the inner sides of which all the junctions are arranged, the latter being protected from the direct action of the gas flame by means of an inner lining of asbestos. The heating is effected by means of gas, and for this purpose a perforated porcelain tube *A*, Figs. 112 and 113, is placed in the cylinder. The gas after passing through a Giroud's regulator *C*, Fig. 112, so as to produce a regular flame under variations of pressure and thus ensure a constant current, is conducted into *A* by the pipe *T* into which air flows through various openings. The mixture of gas and air burns at the perforations in *A*, the further quantity of air necessary for combustion entering from below by the annular space *D* between the pipe *A* and the walls of the cylinder, Fig. 112; the burner is lighted from above, the lid being removed for this purpose.

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* Zeitschr. f. anal. Chem. 11, 4.

† *Ibid.* 15, 334.

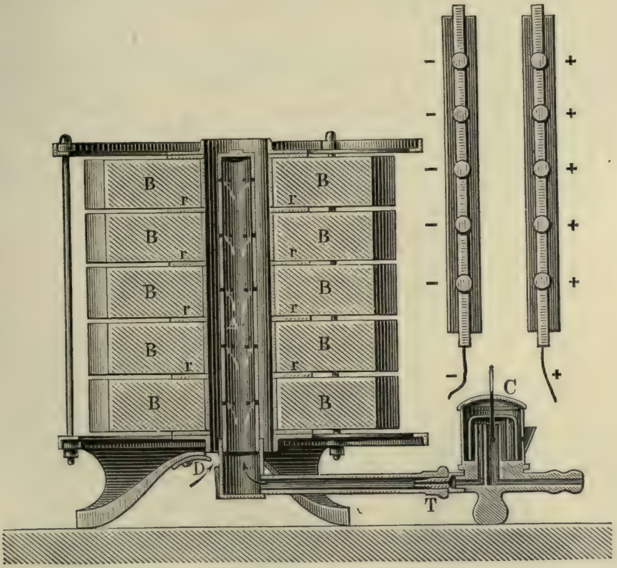

Fig. 112.

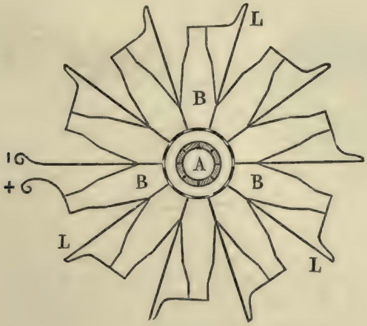

Fig. 113.

The individual elements of a ring are connected in series, but the rings themselves can be made up differently, according to the external resistance. For this purpose, the poles of each ring terminate in binding screws arranged on two vertical metallic strips as shown in the perspective view, Fig. 111. The elements are here shown combined in series, whilst in the sketch plan to Fig. 112 the rings are made up in compound circuit.

b. Form of the Electrodes.

As regards the form of electrode employed in the electrolytic estimation, Luckow at first used a cylinder of platinum foil as the negative electrode and a spiral of strong platinum wire for the positive electrode. Systematic experiments in the laboratory of the Mansfeld Department of Mines at Eisleben have resulted in the adoption of electrodes of the forms depicted in Figs. 114 and 115. The hollow truncated platinum cone weighs 20 grams and is 75 mm. high, 9 mm. in diameter at the top, and 58 mm. at the bottom. The platinum cone is provided with several openings in the sides so as to allow the oxygen liberated on the inner side of the cone to escape to the outer side; this is indispensable in the case of solutions containing much iron, in order to hinder the partial reduction, with a current of sufficient strength, of the ferric oxide to ferrous oxide and of free nitric acid to nitric oxide, and thus avoid the black-brown coloration of the test liquid which would otherwise be produced. The platinum spiral weighs 16 grams.

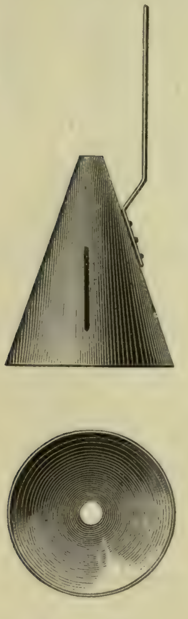
Fig. 114.

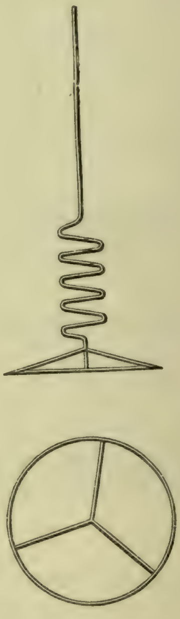
Fig. 115.

In the laboratory of Christofle & Co., of Paris, where—in analysing alloys of arsenical nickel and German silver—it is necessary to work with concentrated solutions, another form of electrode is employed, namely that described by Herpin (*loc. cit.*), and shewn in Figs. 116 and 117. The apparatus consists of a platinum basin *A* supported on a tripod stand *B*, and connected with the negative pole of the battery, the positive electrode being formed by the platinum spiral *C*. To prevent any loss of the substance by the effervescence produced by the escaping gas, the whole is covered by a glass funnel *D*.

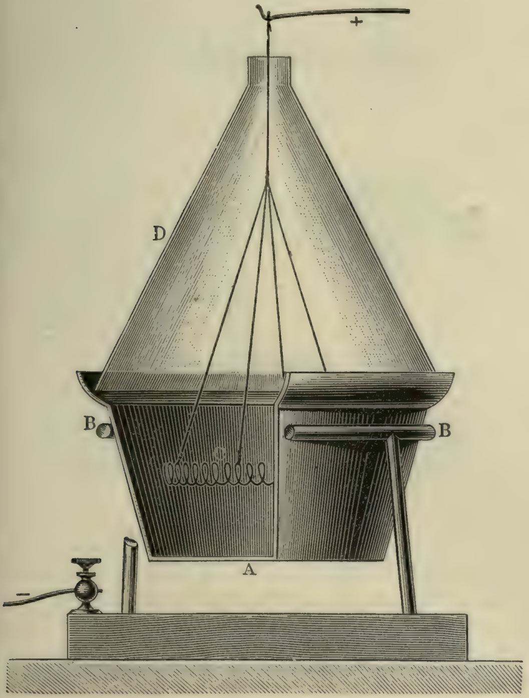

Fig. 116.

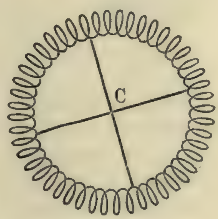

Fig. 117.

A. Classen and M. A. von Reis* also employ as negative electrode a rather deep platinum vessel covered by a clock glass, but for the positive electrode they use a disc of platinum foil of about 45 mm. in diameter which is fastened on to a strong platinum wire by means of a platinum screw.

Riche† when small quantities of liquid are to be electrolised makes use of a platinum crucible which at the same time acts as positive electrode, a platinum cone, Fig. 118, serves as negative pole; this is open at both ends, and rounded so as to correspond in form as nearly as possible with the crucible. Elongated openings are cut in the cone so as to allow of the concentration being uniform during electrolysis. The distance between the cone and the crucible may be 2 to 4 mm. The arrangement is shewn in Fig. 119, and requires no further description, except that the rod *A* is made of a non-conducting material such as glass. If the current is to act in a warm liquid, the crucible is placed in a basin of water to which heat is applied. With larger quantities of liquid the precipitation is effected in a glass beaker; Riche then employs a platinum

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* Ber. deutsch. chem. Gesell. 1881, p. 1623, as also Quantitative Analyse auf elektrolytischen Wege, by A. Classen, Aachen, J. A. Meyer, 1882.

† Ann. de Chim. et de Phys. [v.], 13, 508; Zeitschr. f. anal. Chem. 21, 116.

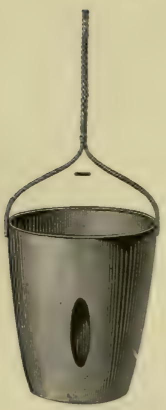

Fig. 118.

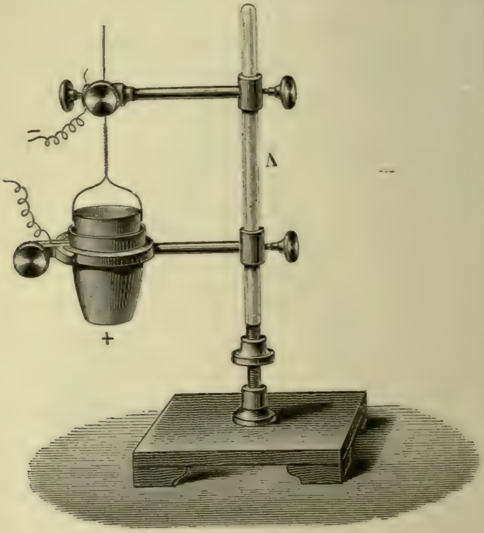

Fig. 119.

cylinder as negative electrode, and for the positive, a piece of platinum gauze bent round into a cylindrical shape, increasing the rapidity of the action by employing, in addition to the platinum gauze outside the cylinder, a supplementary positive electrode consisting of a platinum spiral inside the cylinder.

c. *Dissolving the ore (or lode), and preparing the Solution for Electrolysis.*[*]

a. *If the ores contain no silver.*

The electrolysis is always effected in nitric acid solution; small quantities of free sulphuric acid such as may occur when a nitric acid solution of neutral sulphate of copper is electrolised, are not prejudicial, but hydrochloric acid must not be present, or the copper will not be deposited on the negative electrode (the platinum cylinder) with its usual bright colour, but will be blackish.

If the ores contain bitumen, they must be roasted before dissolving. If nitric acid suffices as the solvent, this acid alone is used, the excess being evaporated, and the residue dissolved by the aid of 20 c.c. of nitric acid of sp. gr. 1·2 made up to 200 c.c. with water. *This volume of liquid and proportion of nitric acid to water must be adhered to for all electrolytic estimations of copper.*

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[*] The following instructions under *c.* are taken from the reports of the Mansfeld Ober-Berg- und Hüttendirection already mentioned, in whose laboratory the electrolytic estimation of copper has been practised for more than twelve years. On p. 393, f., various modifications recommended by others are described.

If nitric acid alone does not suffice, nitric acid, or better, aqua regia is employed with the addition of sulphuric acid.

In the case of ores or lodes rich in copper, 2 grams are taken, the solution being effected in a hemispherical porcelain dish of 14 cm. in diameter and 6 cm. deep, 40 c.c. of nitric acid or aqua regia and 4 c.c. of concentrated sulphuric acid, which must be previously diluted with an equal bulk of water, being employed. The dish is covered with a clock glass during dissolution, this being assisted by warming on a sand-bath. After rinsing the lid into the basin, the contents of the latter are carefully evaporated to dryness, the excess of sulphuric acid driven off, and any sulphur which may have separated is burned off. The residue is dissolved in 20 c.c. of nitric acid of sp. gr. 1·2, diluted with water, and filtered into a beaker 12 cm. high and 8 cm. inside diameter; this, in the first place, has a mark to show to where it is to be filled so as to contain 200 c.c. of liquid, and secondly is provided with an opening 11 mm. wide, and 95 mm. from the bottom, through which the acid liquid can be removed when the electrolysis is complete. After washing the undissolved residue, the solution is diluted up to the mark. If the liquid is required for further estimations after that of the copper, glass beakers are used having a glass tube, bent at right angles, inserted at a distance of 20 mm. below the upper edge.

β. *For ores containing silver.*

If the ore contains silver, this metal, when nitric and sulphuric acids free from chlorine are employed as solvents, will pass into solution completely at the same time as the copper, and will be thrown down and weighed along with it. The quantity present must therefore be separately determined and deducted. If this is not desired, the silver can be removed from the solutions prepared with pure nitric acid alone, by precipitation with an accurately calculated quantity of very dilute hydrochloric acid, 1 c.c. of which is equivalent to 0·001 gram of silver. If nitric acid alone cannot be used as the solvent, aqua regia should be employed, the solution being subsequently evaporated to dryness, and the residue treated with nitric acid, diluted with water, and filtered. The solution, now free from silver, is evaporated to dryness with the addition of sulphuric acid, and the method given in *a*, is followed.

d. Electrolytic precipitation of the Copper.

After the solution has been well stirred, the platinum spiral (the positive electrode) is introduced, and then the platinum cylinder (the negative electrode). The distance of the latter from the base of the spiral should be barely 5 mm. in the case of liquids containing much iron; in solutions very rich in copper the distance may be 10 mm.

Before connecting the electrodes with the pile, it is necessary to ascertain whether the current is of the right strength. In this connection, it should be noted that for samples containing a low proportion of copper, the current should be of such a strength as to yield from 16 to

25 c.c. of oxyhydrogen gas in 30 minutes, on decomposing water acidified with sulphuric acid. If, however, larger quantities of copper are to be deposited, the current required for solutions containing little iron should correspond with a production of 75 to 100 c.c., and for those rich in iron, of 100–120 c.c. of oxyhydrogen gas in 30 minutes. Of course, the current may be measured by a tangent galvanometer instead of by a voltameter.

The deposition of copper on the platinum cylinder begins soon after connection has been made between the electrodes and the thermopile; if it is pure, it exhibits the beautiful light colour of copper and if the current is of the proper strength, the deposit is bright and adherent. The time necessary for deposition varies according to the content of copper, solutions very rich in copper requiring more than 12 hours for complete deposition; in such cases the current must be passed for about 18 hours.

When the deposition appears to be complete, the level of the liquid in the beaker is raised by the addition of water; if the clear portion of the platinum cylinder which was formerly above the liquid, but has now become submerged, exhibits no reddish deposit after the lapse of half an hour, the precipitation is complete. Additional confirmation of this is obtained by withdrawing a sample of the liquid by means of a pipette, and testing it with sulphuretted hydrogen water.

Now, while the current is still passing, a stream of water is introduced at the bottom of the beaker, so as to completely expel the acid liquid, and as soon as the effluent water no longer has an acid reaction the binding screws are loosened and the platinum cylinder is taken out; it is then washed with alcohol, dried at 90–95°, and weighed when cold. The increase in weight is the amount of copper deposited.

e. Procedure in cases where the copper deposited is blackish.

If the copper solution contains arsenic, antimony, selenium, or bismuth, the copper is covered with a brown to blackish deposit, and the accuracy of the results is interfered with. A greyish black, or occasionally peacock, coloration may also occur if traces of hydrochloric acid are present in the solution.

If the elements giving rise to the black deposit are only present in small quantity, and are volatile when heated to redness in air, as is the case when they consist of arsenic, antimony, or selenium, the platinum electrode on which the black deposit occurs is washed with alcohol, dried, and heated to redness over a gas burner or spirit flame or in a muffle. The arsenic and antimony are volatilised, whilst the copper is converted into cupric or cuprous oxide without loss. The platinum cylinder which has been thus treated is now placed in a beaker, a similar, larger, weighed platinum cylinder is suspended over it; the latter is connected with the negative and the former with the positive pole of the battery, and a sufficient quantity of dilute nitric acid (1 pt. of acid to 6 of water) is poured into the beaker. The oxides of copper dissolve, and the copper is thrown down pure on to the outer platinum; it is then determined in the usual way. If the elements giving rise to the black coloration are present in larger quantity, the moment when they begin to deposit on the copper must be watched for, the acid solution at once expelled, and the platinum electrode having only a slight black deposit is treated as described above.

If the copper solutions contain lead, this metal is not deposited with the copper on the negative pole, but as peroxide on the positive pole, and can, if the quantity is not too great, be determined by the increase in weight of the spiral dried at 100°. When larger quantities of lead are present, the lead peroxide adheres in part only to the platinum spiral, the rest separating in thin flakes.

f. Methods differing from those followed in the Mansfeld Works.

Under this section, attention is drawn to a few modifications of the process described above.

α. Wrightson* throws down in ordinary glass beakers, and syphons off the acid liquid while the current is still passing; pure water is then poured in, and the copper spiral, which is not washed with alcohol, is dried at 100 to 120°.

β. A. Classen and M. A. von Reis † deposit the copper from solutions containing it in the form of oxalate of copper and ammonia together with a considerable excess of oxalate of ammonia. For the estimation of large quantities of copper, a current is employed corresponding with the liberation of 330 c.c. of oxyhydrogen gas per hour; this deposits 0·15 gram of copper in about 25 minutes. To separate copper from zinc, A. Classen‡ prefers to precipitate from acid sulphate solutions rather than from nitric acid solutions. Compare also this vol. p. 397 *e*.

γ. Riche§ employs a Bunsen element in the deposition of copper. The sulphuric or nitric acid solution is evaporated almost to dryness, the residue taken up with water, and the liquid electrolysed at 60° to 90°; the copper comes down quickly as a fine red adherent coating. When the deposition is finished, the cone (see this vol. p. 390) is removed from the crucible without interrupting the current, and dipped at once into distilled water; it is then dried at 50° to 60° and weighed. In this way, Riche found that 1 gram of copper was deposited in 3½ hours. In the presence of iron, the decomposition must be conducted at a temperature which should not exceed 70°.

δ. Lecoq de Boisbandran || proceeds as follows for the estimation of copper in solutions containing much ferrous sulphate. For the production of the current, he employs three Bunsen elements weakly charged, a platinum crucible serving as the negative electrode, and a semi-cylindrical piece of platinum foil for the positive. In order to prevent the copper being corroded by the ferric salt formed at the positive pole, which easily takes place in the acid solution, he quickly syphons off the iron solution directly the copper is precipitated, the positive electrode being meanwhile approached very close to the bottom of the crucible so that the passage of the current continues while the liquid is being removed; then, without interruption of the current, the copper is repeatedly washed with dilute sulphuric acid and finally with boiling hot water.

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* Zeitschr. f. anal. Chem. 15, 299.

† Ber. deutsch. chem. Gesell. 14, p. 1627.

‡ Classen's work referred to on p. 389, footnote.

§ Ann. Chim. phys. [v.], 13, 508; Zeitschr. f. anal. Chem. 21, 118.

|| Bull. Soc. Chim. de Paris, 1869, p. 35; Zeitschr. f. anal. Chem. 9, 102.

3. Other Methods for the Estimation of the Copper.

a. F. Mohr* gives the following method for the estimation of copper in ores:—

α. For Oxidised Ores (oxide of copper, cuprous oxide, malachite, phosphate of copper). 5 grams of a rich, or 10 grams of a poor, finely powdered ore is treated in a porcelain dish of 10 cm. diameter with some sulphuric acid, water, and nitric acid, and heated to boiling after the dish has been covered with a large clock-glass. As soon as the mass is nearly dry and ceases to spirt, the clock-glass is removed, and the flame increased. At a high temperature, hydrated sulphuric acid and sulphuric anhydride, from the ferric sulphate, escape, the heat being increased until no more fumes are given off; it is then allowed to cool, distilled water is added, the whole heated to boiling, filtered into a small platinum dish, and washed with hot water, the washings being evaporated and transferred also to the platinum dish; finally—having made quite sure that the residue insoluble in water gives up no copper to acids—the copper is precipitated with zinc, as described in Vol. I. p. 256. The bright-red colour of the copper is an indication of its purity. It will be seen that the object of this process is to remove, as far as possible, the metals precipitable by zinc (lead, antimony, and tin).

β. For Sulphuretted Ores, mixed Metallurgical Products, Ore-furnace Regulus. The substance must be powdered with special care; it is then treated as in *α*, using 5 grams of ore, and heating as before with sulphuric acid, water and a larger quantity of nitric acid. The action must be allowed to go on in the covered porcelain dish at a gentle heat, during which much spirting and condensation of liquid on the clock-glass will take place. A large quantity of sulphur separates, which collects together and envelops some of the powdered ore; the liquid is therefore dried up by applying a stronger heat, the clock-glass is removed, and the heat increased until the sulphur burns, and the free acid is volatilized. When cold, more nitric acid is added and also a very little sulphuric acid; the appearance of red fumes is an indication of the presence of ore still undecomposed. It is again evaporated to dryness as before, allowed to cool, moistened once more with nitric acid, and the sulphur burned off for the second time; in the case of rich ores, this operation has to be again repeated. The extraction of the residue, and the estimation of the copper are performed as in *α*.

b. Storer† and Pearson,‡ with the object of obtaining a solution free from separated sulphur, heat the finely powdered ore, previously mixed with chlorate of potassa, with strong nitric acid on a water bath, and at short intervals add more chlorate of potassa and nitric acid until no more suspended sulphur is perceptible. When cold, strong hydrochloric acid is added in sufficient excess, the whole evaporated to dryness on a water bath, and the residue treated with hydrochloric acid and water, and filtered.

Pearson precipitates the copper with iron, and in order to obtain the solution quite free from nitric acid washes the residue left on evaporation into a beaker with water, heats nearly to boiling, adds about 25 c.c. of a concentrated solution of ferrous sulphate faintly acidified with sulphuric acid and heats for about 5 minutes almost to boiling. If at the end of this time any ferrous salt is still present, which can be ascertained by testing a drop with ferricyanide of potassium, the object is attained; otherwise the heating must be continued with the addition of more ferrous sulphate. Finally the copper, thrown down as metal from the filtered liquid by the introduction of an iron plate, is heated to redness in a porcelain crucible in a current of hydrogen, and weighed.

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* Zeitschr. f. anal. Chem. 1, 143.

† *Ibid.* 9, 71.

‡ *Ibid.* 9, 101.

c. For preparing solutions containing all the copper, various fusion methods can be employed. Fleischer,[*] for decomposing sulphuretted copper ores, recommends fusing the finely powdered sample with a mixture of exactly 5 parts of chlorate of potassa, 4 parts of carbonate of soda, and 3 parts of chloride of sodium, until the mass flows quietly, and dissolving the fused mass in hydrochloric acid and water. W. Gibbs[†] on the other hand recommends to gradually heat the finely powdered ore with 3 to 4 times its weight of a mixture of equal parts of acid sulphate of potassa and nitrate of potassa to a low red heat in a porcelain crucible, preferably in a muffle; in this way oxidation is effected without frothing. The cooled mass is then decomposed with sufficient sulphuric acid to convert all the sulphate of potassa into the acid salt, and carefully heated again until the contents of the crucible are melted to a clear mass, which after cooling is dissolved in water.

d. When all the copper has been brought into solution in one way or another (also as in this vol. p. 382, 2) or by 3 *a*, *b*, or *c*, it may also be estimated *volumetrically*. The older volumetric methods have been already described in Vol. I. pp. 258–262; of new or improved methods the following may be mentioned:

a. F. Weil[‡] supplements his method described in Vol. I. p. 261, by the following special instructions:—5 grams of the mineral is dissolved in hydrochloric or sulphuric acid free from nitric acid, and diluted to 250 c.c., 4·5 to 5 grams of crystallised stannous chloride is dissolved in about 100 c.c. of water, with the addition of about 30 c.c. of hydrochloric acid, and the solution diluted to 500 c.c. with a mixture of about 40 c.c. of hydrochloric acid and 100 c.c. of water. A normal solution of copper, containing 0·1 gram of copper per 10 c.c., is also prepared. To determine the effective value of the stannous chloride solution, this is allowed to act, in a flat bottomed flask, on 10 c.c. of the normal copper solution to which 25 c.c. of hydrochloric acid has been added, the whole being heated to boiling.

In a similar way, the stannous chloride solution is allowed to act on 10 c.c. of the solution of copper ore, also mixed with 25 c.c. of hydrochloric acid, and heated to boiling. If it has been necessary to use nitric acid or aqua regia in order to make the solution, the latter must be evaporated to dryness, and the residue dissolved in hydrochloric acid, and diluted to 250 c.c.; 10 c.c. of the solution are removed by a pipette, evaporated to dryness along with 5 to 10 c.c. of hydrochloric acid, and the residue, now certainly free from nitric acid, is dissolved in 25 c.c. of hydrochloric acid and the process carried out as above. The circumstance, that during titration at the boiling temperature, the flask is full of the vapours of hydrochloric acid, prevents oxidation by atmospheric air.

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[*] Zeitschr. f. anal. Chem. 9, 258.

[†] *Ibid.* 7, 257.

[‡] *Ibid.* 17, 438; Procédés F. Weil's pour le dosage vol. du cuivre, du fer, et de l'antimoine.

The method to be employed when the copper solution contains ferric chloride or sulphate, has already been described in Vol. I. p. 261.

If the ore contains antimony, dissolution is effected by means of hydrochloric acid or a mixture of much hydrochloric acid with a little nitric acid, permanganate of potassa being added until there is a permanent red tinge, and it is then heated to boiling until the red coloration disappears and the evolved vapours no longer turn iodide of potassium starch-paper blue. The solution is now diluted to 250 c.c. with an aqueous solution of tartaric acid containing 5 to 10 per cent. of the acid, or with water to which the requisite amount of hydrochloric acid has been added. The solution contains the copper as chloride, and the antimony as antimonic acid. If 10 c.c. of the solution, mixed with 25 c.c. of hydrochloric acid and heated to boiling, is submitted to the action of the titrated stannous chloride solution, the copper is reduced to cuprous chloride and the antimony pentachloride to trichloride, the volume of stannous chloride employed showing the quantity of copper and antimony present; according to the equations:

$$SbCl_5 + 2SnCl = 2SnCl_2 + SbCl_3 \text{ and } 4CuCl + 2SnCl = 2SnCl_2 + 2Cu_2Cl$$

Under the given conditions, the reducing effect of the stannous chloride solution is the same for 4 equiv. of copper ($4 \times 31{\cdot}7 = 126{\cdot}8$) as for 1 equiv. of antimony (122). In order to ascertain the amount of copper alone, the reduced liquid is exposed to the air for 12 hours in a shallow porcelain basin, whereby all the cuprous chloride is reconverted into cupric chloride. If the titration with stannous chloride is repeated, the amount of the copper is ascertained from the difference between the volume of stannous chloride employed, and the amount of it corresponding with the antimony; and from this the quantity of the latter can be found. Arsenic acid, according to Weil, is not reduced during the short time required for the titration.

β. Volhard* estimates the copper volumetrically by precipitating it as cuprous sulphocyanate and estimating the excess of sulphocyanate of ammonium solution (see the method of silver estimation on the same basis, this vol. pp. 361 and 362). He employs decinormal solutions, a solution of nitrate of silver containing 10·793 grams of silver per litre, and a solution of sulphocyanate of ammonium of a strength so proportioned to that of the silver solution that on mixing equal volumes of the two in the presence of ferric sulphate, there is a barely perceptible coloration; 1 c.c. of the sulphocyanate of ammonium solution corresponds with 0·00634 grams of copper.

The copper is dissolved in sulphuric or nitric acid and the excess of acid removed by evaporation; if the excess is not very large, it may be neutralised by adding carbonate of soda until there is a permanent turbidity. The solution to be titrated is placed in a 300 c.c. measuring flask, an aqueous solution of sulphurous acid is added until the liquid smells strongly of it, whereby any precipitate of basic carbonate of copper which may have been produced is dissolved, the whole is heated to boiling, and the sulphocyanate solution added from a burette until the addition of more produces no alteration in the colour. To make sure, 3 or 4 c.c. more are run in and the total quantity noted. The solution containing the nearly white precipitate of cuprous sulphocyanate is allowed to cool, the flask filled with water up to the mark, and the whole mixed, and filtered through a dry filter into a dry flask; 100 c.c. of the filtrate is taken out with a pipette, 10 c.c. of a cold saturated solution of iron ammonium alum and a little nitric acid are added, the mixture titrated with silver solution until the solution becomes colourless, and then sulphocyanate of ammonium solution is carefully added from a pipette or burette graduated to $\frac{1}{20}$ths of a c.c. until the liquid acquires a permanent reddish tinge. The number of c.c. of silver solution employed (after deducting the sulphocyanate solution used in re-titrating) multiplied by 3 and deducted from the amount of sulphocyanate solution originally added indicates the number of c.c. of sulphocyanate solution required for the precipitation of the copper.

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* Zeitschr. f. anal. Chem. 18, 285.

In the presence of iron, the point of complete precipitation of the copper cannot be recognised by the absence of a change of colour. The ferric oxide gives rise—even when all the copper is precipitated—to a dark coloration of the sulphocyanate solution where it falls into the liquid, but, on shaking, this disappears through the action of the sulphurous acid. In this case, in order to ascertain when the precipitation of the copper is complete, some of the fairly clear solution above the precipitate must be transferred to a test tube and warmed, a drop of sulphocyanate solution being run in from the burette; if the turbidity does not increase all the copper has been thrown down. The sample is then returned to the main bulk of the solution and the process carried out as already described. This method is not available in presence of the halogens, of silver, or of mercury.

e. Classen * employs the oxalic acid method, already described for zinc (this vol. p. 278) and nickel (this vol. p. 303), for estimating copper in solutions which, as in the case of solutions of copper ore, contain ferric chloride, chloride of antimony, chloride of arsenic, &c. If but little antimony is present, the nitric acid solution is evaporated to dryness, an excess of concentrated oxalate of potassa solution added, the whole filtered hot, and the residue washed with water to which oxalate of potassa has been added. The filtrate is concentrated to 50 c.c. or so, whereby nearly the whole of the copper separates in blue needles consisting of oxalate of copper and potassa, 2 volumes of about 80 per cent. acetic acid are added, and the mixture is allowed to remain for a time. It is then filtered, the precipitate washed with a mixture of concentrated acetic acid, alcohol, and water in equal volumes, dried, and heated to low redness in a platinum crucible; the residue is dissolved in sulphuric acid, and the copper deposited electrolytically, whereby it is obtained free from zinc, nickel, magnesium, &c.

If antimony is present in considerable quantity, as well as arsenic, the finely powdered substance, or the residue left on evaporating the solution, is mixed with about four times the quantity of chloride of ammonium and heated *very gently* in a covered crucible. In this way, nearly all the arsenic and antimony, together with a good deal of ferric chloride are volatilised. The copper can be estimated in the residue in the manner already described.

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* Zeitschr. f. anal. Chem. 18, 390 and 391.

B Varieties of Copper.

I CEMENT COPPER.

§ 262.

Since Spanish pyrites containing copper has been so largely used, particularly in the manufacture of sulphuric acid, and cement copper has been prepared from the waste, this cement copper has come into the market in large quantities; and, as it exhibits great variations both in the amount of copper and degree of moisture, it is often the subject of analysis. The commercial qualities are, as a rule, fine, homogeneous, and either red, containing about 5 to 15 per cent. of moisture, or, if precipitated by cast iron instead of wrought iron, or if freed from water by heating, they are black, and in this case almost free from water. Occasionally cement coppers are met with consisting partly of fine, partly of medium powder, together with larger lumps of copper. The homogeneous and irregular kinds require to be treated differently if the result of the analysis is to indicate their average composition.

1. Fine, homogeneous, red or black, Cement Copper.

a. Estimation of Water.

About 75 grams of the cement copper, uniformly mixed, is dried at 100° until the weight is constant; for this purpose, a semicylindrical box of tinplate is used like that shown in Fig. 120, 160 mm. long, 40 mm. wide, and 22 mm. in depth, provided with a sliding lid;* this, without the cover, is inserted in a slightly wider copper tube which is fixed crosswise and slightly inclined in a box-shaped copper water bath so as to be completely surrounded by boiling water or steam at 100°. After a few hours, the box is taken out of the tube, closed with its lid, cooled in a dessicator, and weighed; after again removing the lid, it is replaced in the tube, heated for an hour and again weighed to see if the weight remains constant; as soon as this is the case, the estimation is finished.

Fig. 120.

b. Estimation of the Copper.

About 60 grams of the cement copper which has been dried at 100°, or, if the water estimation and the dissolution are to be carried out simultaneously, of the undried copper, is treated with hydrochloric acid of sp. gr. 1·12, to which nitric acid is added gradually, heating at the same time until there is no longer any action; the solution is then diluted, and filtered into a tared two litre measuring flask. The undissolved washed residue, which is mostly carbonaceous, after being heated to redness with access of air until all the combustible matter is burnt off, is treated at a gentle heat with hydrochloric acid with addition of nitric acid, diluted, and the solution filtered into the main solution; when cold, it is filled up to the mark, well mixed, and weighed. The copper is now estimated in aliquot parts of this solution. The method about to be described allows all the extraneous metals which may be present to be separated, and therefore under any circumstances gives thoroughly trustworthy results. It will be easily understood that one of the simpler methods of copper estimation given in § 261, II. may be employed, but it should always be borne in mind that the impurities (lead, antimony, iron, &c.) which may be present in cement copper may affect the accuracy of the results.

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* The author uses this box not only for estimating the water in cement copper, but also for the determination of moisture in mineral or other substances of which it is necessary to take tolerably large quantities in order to arrive at a correct average of the amount of moisture.

α. Thirty c.c. of the solution is measured out with a pipette and transferred to a light, stoppered glass (which has been accurately weighed along with its stopper) and weighed. Here the weight of the solution is the sole point of determination, the object of the measuring being merely to enable one to take a suitable quantity of the solution for analysis.

β. The contents of the weighing glass are rinsed with water into a flask of 400–500 c.c. capacity, 20 c.c. of hydrochloric acid of 1·12 sp. gr. is added, and the mixture precipitated with sulphuretted hydrogen while hot, the precipitate being collected and washed with water to which a little sulphuretted hydrogen water and acetic acid have been added. The washing is complete when the filtrate, on adding ammonia and sulphide of ammonium to it, no longer gives a precipitate of ferrous sulphide or any coloration.

γ. The precipitated sulphide of copper, together with the filter, is transferred to a beaker, 10 to 20 c.c. of sulphide of sodium solution and about 50 c.c. of water are added, the mixture heated for five minutes, diluted with about 100 c.c. of water, filtered, and the precipitate washed with water to which a little sulphide of sodium solution has been added. The filtrate and washings are now acidified with hydrochloric acid so as to be certain that the sulphur which separated contains no sulphide of copper, which is at once recognisable from the colour of the precipitate.

δ. The sulphide of copper together with the filter is put back into the beaker in which the treatment with sulphide of sodium was effected, 20 c.c. of nitric acid of sp. gr. 1·2, and 20 to 30 c.c. of water are added, the whole warmed until the sulphide of copper dissolves, diluted, filtered into a flask and the filter washed. The dried filter is then carefully incinerated in a porcelain crucible, and the residue, after being warmed with a little hydrochloric and nitric acids, is diluted and filtered into the other solution. Should this yield a slight turbidity resulting from the separation of a small quantity of chloride of silver, it must be left to settle and then filtered; this, however, is, as a rule, unnecessary. Ammonia is now added to the clear or filtered solution until it is faintly alkaline, then carbonate of ammonia; the whole is allowed to remain 12 hours at a moderately warm temperature, filtered, the filtrate acidified with acetic acid, precipitated hot with sulphuretted hydrogen, and the copper estimated as cuprous sulphide, as in Vol. I. p. 257.

ε. Should the cement copper contain a relatively large amount of lead, it is preferable to separate this by adding an excess of dilute sulphuric acid to the nitric acid solution obtained at the commencement from the evaporated weighed quantity.

2. Non-homogeneous Cement Copper.

If a cement copper consists of portions of very unequal character, that is fine powder, moderately fine powder, and coarser lumps, an average sample cannot be obtained by simple mixture.* In such a case, after determining the amount of moisture in the whole sample, the different qualities must be separated by sifting, each grade being again dried at 100°, weighed separately, and an aliquot part, say $\frac{1}{10}$th of each, weighed off carefully and used for preparing the solution. In the case of the cement copper referred to in the footnote, a sample weighing 4358·7 grams, consisted of 3197·5 grams of fine powder, 747·0 of medium powder, and 414·2 grams of lumps. One-tenth of each was weighed out, and the sample thus obtained weighing 435·87 grams was dissolved in nitric acid; the solution weighed 7845·3 grams, and the copper was estimated in weighed aliquot parts thereof.

II. COARSE COPPER, REFINED OR TOUGHENED COPPER.

§ 263.

Although in the analysis of cement copper, an estimation of the copper alone is generally sufficient, in the case of coarse copper it is necessary to make determinations of all the constituents. The difficulty of carrying out such an analysis increases with the number of foreign substances to be estimated, mostly present in very small quantities, and in order to form an opinion on the copper, it is not sufficient merely to know what they are and their amount, but the manner in which they are combined in the copper must also be ascertained; this problem was first solved by the comprehensive investigation which was carried out with extreme care by W. HAMPE.†

The foreign elements which usually occur, or may occur, in coarse copper, are the following, namely, silver, gold, arsenic, antimony, tin, bismuth, lead, iron, cobalt, nickel, zinc, sulphur, phosphorus and oxygen.

In the following paragraphs two methods are first described which are suited for the quantitative determination of these elements, which altogether usually amount only to about 0·5 to 1·0 per cent.; then the way in which the mode of combination of the various foreign elements present is ascertained.

a. First Method, in which the Copper is not electrolytically precipitated.‡

1. 100 grams of the carefully cleaned copper is treated with a quantity of perfectly pure nitric acid of sp. gr. 1·20, sufficient to dissolve

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* See the author's communication on this point in Zeitschr. f. anal. Chem. 15, 63.

† "Beiträge zur Metallurgie des Kupfers," Zeitschr. f. Berg-, Hütten-, u. Salinenwesen, 27, 205; Zeitschr. f. anal. Chem. 13, 176.

‡ See the author's paper in the Zeitschr. f. anal. Chem. 21, 229.

it (water being added in the case of copper turnings), and until, even when warmed, there is no longer any action; it is then diluted with water, filtered, and the insoluble residue washed; the filtrate is collected in a tared 2-litre measuring flask, filled up to the mark and mixed.

2. The residue is rinsed into a porcelain basin, the filter ash added, and the whole, after evaporation to dryness, is transferred to a porcelain crucible, any adherent particles being removed by rubbing with some carbonate of soda which is also introduced into the crucible; flowers of sulphur is then added, the mixture fused with exclusion of air, and after cooling treated with water, the yellow solution being filtered from the black residue, and the latter washed.

3. The black residue left in 2 is treated, together with the filter, with moderately dilute nitric acid, filtered, and washed; the filter is now burned, the ash heated with nitric acid, diluted with water, filtered, and the filtrate added to the first solution; this second filter is also incinerated, and the filter ash reserved as it may contain a part of the gold. A little hydrochloric acid is now added to the solution; if a precipitate of chloride of silver is formed, it is allowed to settle, collected and the chloride converted into *silver* before weighing; finally testing its purity. The clear liquid, or the solution filtered from the chloride of silver, is evaporated with sulphuric acid to separate the *lead;* the *copper* and *bismuth*, when present, are precipitated from the filtrate by sulphuretted hydrogen, any metals of the fourth group being thrown down in the filtrate from this by means of sulphide of ammonium.

4. The sulphide of potassium solution from 2 is precipitated with hydrochloric acid and filtered. The precipitate, which contains much admixed sulphur, is treated, together with the filter, with hydrochloric acid containing bromine, until everything soluble is dissolved; it is then filtered, washed, any free bromine removed by means of ammonia, acidified with hydrochloric acid, and precipitated at 70° with sulphuretted hydrogen. The metallic sulphide is collected on a filter, dissolved in weak yellow sulphide of ammonium, filtered, and the solution evaporated to dryness in a porcelain crucible; the residue is carefully oxidised with fuming nitric acid, evaporated to dryness, hydrate of soda added together with a small quantity of nitrate of soda, the whole fused, and the separation of the *antimony*, *tin*, and *arsenic*, if they are all present together, is effected according to H. Rose's method, described in Vol. I. p. 487 (**201**). The filter, through which the solution of the metallic sulphides in sulphide of ammonium and the antimoniate of soda dissolved by the hydrochloric and tartaric acids have been filtered, is incinerated after washing, and the ash, to which is added the one kept back above (see 3), is treated with aqua regia. It is then diluted, filtered, evaporated with hydrochloric acid to remove the nitric acid, and the gold present is precipitated from the solution by ferrous chloride after it has been evaporated to a small bulk.

If tin is not present, the *antimony* and *arsenic* are more conveniently separated by Bunsen's method (see this vol. pp. 352 and 353) in the solution in brominated hydrochloric acid, after removing the free bromine by ammonia. The weighed metallic sulphide must, however, be tested for gold.

5. The *copper* is estimated in about 20 grams of the solution from 1, according to the method described for cement copper (this vol. p. 398).

6. To one litre of the liquid from 1, corresponding with 50 grams of copper, four drops of hydrochloric acid are added; if a turbidity or precipitate of chloride of silver is produced, this is allowed to settle in a warm place, and a few drops more of hydrochloric acid are added, to see if all the silver has been thrown down. Should a further turbidity occur, a drop or two more of hydrochloric acid is added, but any considerable excess must be avoided. It is best to convert chloride of silver into metallic *silver* for weighing. The amount obtained, when multiplied by two, and added to that found in 3, gives the percentage of silver.

7. The liquid in 6, which has remained clear on adding the hydrochloric acid, or that filtered from the chloride of silver, is transferred to a porcelain basin, 85 grams of pure concentrated sulphuric acid, previously diluted with water is carefully added, and the whole evaporated until all the nitric acid is driven off; water is added, and the mixture warmed until all the sulphate of copper is dissolved, the liquid being filtered into a 2 litre measuring flask. The insoluble residue of sulphate of *lead* is washed first with water containing sulphuric acid, then with spirits of wine (which must be collected apart), weighed (Vol. I. p. 244) and tested as to purity by boiling it with a solution of acetate of ammonia containing some free ammonia; if an insoluble residue is left even after repeated boiling, it should be freed from sulphate of lead and tested further.

8. The solution from 7, filtered off from the sulphate of lead is made up to 2 litres, mixed, and 500 c.c. placed in each of 4 flasks holding about 1½ litres.* The contents of each flask is diluted with about ½ a litre of water, 50 c.c. of hydrochloric acid of sp. gr. 1·12 is added to each, the mixture heated to about 70°, and the copper, &c., precipitated with sulphuretted hydrogen. When cold, the contents of the four flasks are transferred to a weighed glass stoppered flask of about 6 litres capacity, the flasks being rinsed out repeatedly with sulphuretted hydrogen water so that the whole of their contents are brought into the large flask, the liquid is mixed well, and the flask weighed. The weight of the solution in the flask is ascertained by deducting from the total weight, the tare of the empty flask, and also the weight of the sulphide of copper, which can be calculated from that of the copper. When the precipitate has settled, the supernatant liquid is drawn off from it as far as possible, and the flask with the precipitate and the remainder of the solution is weighed; this gives the weight of liquid removed. The latter is filtered, evaporated in a porcelain basin until by far the greater part of the sulphuric acid is evaporated, heating finally with a little nitric acid, adding ammonia, filtering, dissolving the precipitate in hydrochloric acid, precipitating again with ammonia and estimating any *iron* in the precipitate, according to Vol. I. p. 435 (**77**). After adding acetate of ammonia to the filtrate and acidifying with acetic acid, the *nickel*, *cobalt* and *zinc* are precipitated and estimated and separated as described in this vol. pp. 276, 301 and 302. Finally, the amounts of iron, nickel, cobalt and zinc obtained must—as they come from only a part of the solution drawn off from the sulphide of copper—be calculated to the whole.

9. To the precipitate, together with the remainder of the solution

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* The reason for advising the contents of each boiling flask to be measured is that in case of accident to one of them the labour may not be entirely wasted.

left in the large flask, potash or soda solution is added until the liquid has a strongly alkaline reaction, then a solution of sulphide of potassium or sodium containing some bisulphide in quantity sufficient to be certain of dissolving all the sulphides of antimony and arsenic, and the whole is warmed gently for some time. It is then diluted largely with water, mixed, weighed, as much of the liquid as possible is removed, and the flask with the precipitate and the remainder of the solution is weighed, thus giving the amount of liquid removed. The latter is filtered, acidified with hydrochloric acid and allowed to settle. From the explanation given in 8, it follows that the amount of copper which corresponds with the metallic sulphides of the sixth group precipitated from the alkali sulphide solution can be easily calculated. As these sulphides are mixed with a large excess of sulphur, the precipitate, after settling, is collected, washed, treated while still moist with hydrochloric acid containing bromine, diluted, filtered, and ammonia added until the solution is colourless; then, after gently heating for a long time, hydrochloric acid is added. The metals of the sixth group are now precipitated from the clear solution by sulphuretted hydrogen, and separated as in 4. The results must be reckoned from the part to the whole.

10. The precipitate of sulphide of copper separated from the main bulk of the liquid in 9 containing the alkali sulphide, is now thrown on to the filter through which the liquid has been filtered, washed with water containing sulphide of potassium or sodium, and dissolved in hydrochloric acid with the addition of nitric acid; it is then filtered, evaporated to dryness on the water bath with the addition of hydrochloric acid in excess, and the saline mass extracted with water and filtered after long standing. The insoluble residue, which contains all the bismuth as basic chloride, is dissolved in hydrochloric acid, potash solution is added until alkaline, then cyanide of potassium in slight excess and sulphide of potassium; in this way, the *bismuth* is thrown down as sulphide, whilst the copper associated with it remains in the solution. As the sulphide of bismuth may also contain sulphide of nickel, it is dissolved in nitric acid, the dilute solution precipitated by sulphuretted hydrogen, and the now pure sulphide of bismuth estimated either as such (Vol. I. p. 264, 3) or by converting the sulphide of bismuth into the oxide.

11. Ammonia is added to 400 c.c. of the solution obtained in 1, corresponding with 20 grams of copper, until the greater part of the free nitric acid is neutralised, then a few drops of a solution of nitrate of baryta, and the whole is allowed to remain in a warm place for a considerable time. If the copper contains any considerable traces of sulphurous acid (any *sulphur* present in rough copper is in this state, HAMPE[*]), a slight precipitate of sulphate of baryta is formed, and this must be collected and estimated. Very slight traces of sulphurous acid cannot however be detected in this way, as sulphate of baryta is not absolutely insoluble in the nitrate of copper solution. To detect very slight traces, the copper (about 30 to 40 grams) must, according to HAMPE,[†] be treated in a current of pure and dry chlorine and the sulphuric acid estimated in the volatile products. For this purpose, the copper is introduced into a tube of refractory Bohemian glass which at the exit is bent, first downwards and then upwards, and is placed so that it slopes

[*] Zeitschr. f. anal. Chem. 13, 222.

[†] *Ibid.* 13, 223.

towards that extremity; to the exit is attached a PELIGOT'S bulb-tube, which in its turn is connected with a second. Vulcanised india-rubber must be entirely excluded in setting up this apparatus. The PELIGOT tubes are partly filled with water which has been saturated with chlorine before the commencement of the operation. In order that the chlorine may be pure and free from moisture, it must be well washed, and dried by passing it over chloride of calcium. When the apparatus is adjusted, the copper is warmed for a short time; it then glows as it unites with the chlorine to form cuprous chloride which runs down into the lower, bent portion of the tube. As soon as only a little copper is left unattacked, the tube is warmed again and the current of gas is moderated at the same time. At the termination of the experiment, the contents of the receivers are united and heated until the chlorine is removed, the sulphuric acid being determined by chloride of barium.

For other methods of estimating the sulphurous acid occurring in refined copper see 13.

12. 400 c.c. of the solution from 1, after being repeatedly evaporated with hydrochloric acid to remove the nitric acid, is diluted with about 1200 c.c. of water, precipitated at 70° with sulphuretted hydrogen, the whole transferred to a weighed flask of a capacity of about 2 litres, rinsed, mixed, and weighed. It is then allowed to settle, as much of the supernatant liquid as possible drawn off, the flask, precipitate, and remainder of the solution weighed, and the amount of copper corresponding with the liquid which has been removed is calculated (see 8). The clear liquid is filtered, evaporated to a small bulk with repeated additions of nitric acid, and any phosphoric acid, arising from *phosphorus* contained in the copper, is estimated according to Vol. I. p. 307, β.

13. For estimating the *oxygen* contained in rough copper, &c., which, according to HAMPE (*loc. cit.*) is combined, partly with copper as cuprous oxide, partly with other metals as oxides and acids, and partly with sulphur as sulphurous acid, the following method described by HAMPE,* yields very accurate results, if all the precautions are observed, but not otherwise.

The quite bright copper, reduced to filings with a not too coarse-grained file, is sifted through a hair sieve, any particles of iron which may be mixed with them are extracted by a magnet, and the powdered copper is boiled in dilute potash solution, whereby any traces of fat are dissolved and paper fibres are washed away. The copper purified in this way is thoroughly washed, and dried rapidly.

The estimation of the oxygen in it is effected by ascertaining the loss in weight which the powdered copper undergoes when heated to redness in hydrogen. A Bohemian glass bulb-tube drawn out at both ends serves for the reduction. This is heated in a current of dry air, allowed to cool in it, and then both ends are closed by small caoutchouc tubes, stopped by glass rods; it is weighed, the dry copper powder (about 30 grams) is introduced into the bulb, and the whole weighed again. Thoroughly purified dry carbonic acid is now passed through the tube, the carbonic acid being evolved from hydrochloric acid and marble † in a constant apparatus. The generating apparatus must be set in action 2 hours before it is required for use, and in order to purify and dry the carbonic acid it is passed first through a solution of bicarbonate of sodium, then through a tube containing lumps of the salt, a wash-bottle containing a solution of nitrate of silver, a tube filled with pieces of pumice soaked with the same solution, a flask containing concentrated sulphuric acid, and finally through a tube filled with porous chloride of calcium. After the carbonic acid has passed through the bulb-tube containing the copper for about 5 minutes, the latter is heated very moderately in order to remove all traces of moisture; no combustible products should in this case be evolved. Too strong heating of the copper should be avoided, as otherwise, if the copper contains salts of arsenic acid, a sublimate of arsenious acid may be formed.

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* Zeitschr. f. anal. Chem. 13, 202.

† The air contained in marble can be easily removed, according to A. BERNTHSEN (Zeitschr. f. anal. Chem. 21, 63), by covering the lumps with water in a thick

After allowing it to cool in the current of carbonic acid, the latter is displaced by dry air, and the tube closed and weighed; the difference between this and the former weight will only be a few milligrams. A very slow current of pure hydrogen is now passed over the copper filings, which are heated slowly at first, and subsequently until the whole of the copper is thoroughly red hot, this temperature being maintained for 15 minutes. Water is formed during the heating, and in the case of impure copper a black sublimate of arsenic, antimony, and lead, may be deposited in the upper part of the bulb and close behind it; on this account the end of the tube must be sufficiently long and the current of hydrogen so slow that none of the sublimate whatever may leave the tube.

With copper which contains sulphurous acid, some sulphuretted hydrogen is evolved with the water vapour. As the amount of this must be ascertained, the evolved gas is passed through an alkaline lead solution or through hydrochloric acid containing bromine, and estimated as in this vol. p. 331.* After the copper has been thoroughly cooled in the current of hydrogen, and the latter displaced by dry air, the tube is closed and weighed. The loss in weight, less that of the sulphur evolved as sulphuretted hydrogen, gives the amount of oxygen.

b. Second Method, Electrolysis being employed for precipitating the Copper, HAMPE.†

1. For the main analysis, the copper is used in clean chiselled pieces, two portions of 25 grams each being weighed out. Each is treated in a beaker with a mixture of 175 to 180 c.c. of nitric acid of sp. gr. 1·2 and 200 c.c. of water at a gentle heat until everything which is soluble is dissolved; each portion of liquid is then evaporated to dryness on a water bath, without previously filtering off any insoluble residue and after adding 25 c.c. of pure concentrated sulphuric acid previously diluted with water; it is finally heated more strongly until all the free sulphuric acid is volatilised. Each of the completely cooled basins is covered with a clock-glass, and 20 c.c. of nitric acid of sp. gr. 1·2 is carefully added, and then, gradually, 350 c.c. of water; when all the sulphate

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flask and exhausting the latter by means of a water-pump or some other kind of air-pump.

* The amounts of sulphur thus obtained agreed (in the results published by HAMPE: Zeitschr. f. anal. Chem. 13, 226) fairly well on the whole with those obtained by heating the copper in a current of chlorine.

† Zeitschr. f. anal. Chem. 13, 180.

of copper is dissolved, an accurately measured quantity of titrated hydrochloric acid (1 c.c. = 0·001 gram of silver) is added in order to exactly precipitate the silver present, the quantity of which has previously been ascertained by scorification and cupelling (this vol. pp. 366 and 367). The mixture is allowed to remain for 24 hours and the precipitate, consisting of sulphate of lead, chloride of silver and antimonic acid or its salts, is filtered through small filters, thoroughly washing both the basins and filters. The precipitates are designated I. *a* and *b*. The basins are rinsed out with hot concentrated hydrochloric acid to remove adherent particles of antimonic acid, both solutions are united, diluted with water, and precipitated by sulphuretted hydrogen, and both the liquid and the precipitate of sulphide of antimony, &c., which may be called II., are kept for the present.

2. The copper solutions from 1 and the washings, each measuring 400–450 c.c., are placed in separate glasses 9·2 cm. wide and 15 cm. high, and the copper thrown down by electrolysis (this vol. p. 391). The current must be sufficiently strong to liberate 130 c.c. of oxyhydrogen gas from dilute sulphuric acid (1 : 22) in 30 minutes, and it is important to maintain the current approximately at this strength. The precipitation of the copper from the solution will take about 72 hours. When the liquid has become colourless or nearly so, and only a trace of copper is deposited by the action of the current on a portion of the platinum cone freshly immersed, the liquid is run off into a large flask holding about 4 litres, without interrupting the current, and washed out until the evolution of gas from the positive pole ceases, and the water therefore is no longer acid. The current is now stopped and the cone with the deposited copper is washed first with water and then with spirits of wine, dried quickly (best by suspension in the hot current of air arising from a large platinum or silver dish heated from below), and the *copper* weighed. The two estimations of copper carried out in this way are a mutual check. If the copper is of a bright pure colour, it is a sure proof that no antimony or arsenic has come down along with it, as would be the case if the current were allowed to pass after the copper is entirely deposited. As the copper has still to be tested for bismuth (this vol. p. 408, 8), it must be set aside for the present.

3. The syphon and platinum spirals used in 2 are rinsed with water into the large flask, the small quantity of peroxide of lead adhering to the platinum spirals is dissolved in hot hydrochloric acid over one and the same porcelain basin, the solution (which contains also a little platinic chloride) evaporated to dryness with hydrochloric acid, the residue heated to redness, and the sulphate of lead dissolved in hot hydrochloric acid; ammonia is now added until the liquid is alkaline, then nitric acid until it is just acid, the whole precipitated by sulphuretted hydrogen, and the liquid and precipitate, which we will call III, reserved for the present.

4. The liquid in the large flask, obtained in 2, is boiled in the flask and then evaporated in a porcelain basin, at first over the water bath, and finally at a higher temperature until almost all the free sulphuric acid is driven off, and only a few drops of liquid remain in the basin. When cold, concentrated hydrochloric acid is added, the mixture warmed, diluted, the small quantity of silicic acid derived from the vessels is filtered off, and the filtrate saturated with sulphuretted hydrogen; after being allowed to remain 24 hours at 75°, the saturation with the gas is

repeated and the excess of it driven off at a gentle heat, thus ensuring the complete precipitation of all the arsenic. The following are now filtered through a suitable filter:—*a*, the precipitate of plumbic sulphide III (see 3); *b*, the precipitate of sulphide of antimony, &c., II (see 1); and *c*—after previously removing the filtrates from III and II—the precipitate produced by sulphuretted hydrogen in the electrolysed liquid. This precipitate is thoroughly washed but not dried (it is called IV), the filtrate is, however, concentrated until all the sulphuretted hydrogen is driven off, boiled with a little nitric acid, and ammonia added in excess. If a precipitate of ferric hydrate is produced, this is redissolved in hydrochloric acid, precipitated again with ammonia, and the ferric oxide weighed, the gravimetric estimation of the *iron* being checked by a volumetric analysis. The *nickel* and *cobalt* are precipitated electrolytically from the ammoniacal solution (this vol. p. 304) and separated by means of nitrite of potassa (Vol. I. p. 443, 9).

5. The precipitates I. *a* and *b* (see 1), are removed as completely as possible from the filters, the latter are treated with fuming nitric acid in a porcelain crucible, and the whole evaporated to dryness and cautiously heated, a little nitrate of ammonia being added so as to completely destroy the organic matter; when cold, the precipitates which were removed from the filters are shaken into the crucible and the contents fused with three parts of a mixture of carbonate of soda and sulphur, excluding the air as much as possible. The fused mass is left in water to disintegrate completely, the hot, yellow solution is filtered through the filter containing the still moist precipitate IV (see 4), and washed first with dilute sulphide of potassium solution, and then with sulphuretted hydrogen water. The filtrate contains all the arsenic, antimony and tin (also any traces of gold which may be present in the form of sulphur salts); whilst the precipitate (V) contains the whole of the lead and silver and the portions of bismuth and copper here present.

6. The solution of sulpho-salts obtained in 5 is precipitated by dilute sulphuric acid, collected, the precipitate dissolved in freshly prepared sulphide of ammonium, and the solution evaporated to dryness. If only *antimony* and *arsenic* are present, the residue is heated with hydrochloric acid and chlorate of potassa, tartaric acid is added and then ammonia, and the whole filtered. The arsenic acid in the filtrate is precipitated with magnesia mixture, collected after long standing, dissolved in hydrochloric acid, reprecipitated by ammonia, and weighed as ammonia magnesia arsenate (Vol. I. p. 283, 2); or it may be dissolved in hydrochloric acid, and the arsenic precipitated by sulphuretted hydrogen, the magnesia in the concentrated filtrate being estimated (Vol. I. p. 190, 2), and the amount of the arsenic acid calculated therefrom. The latter method is recommended by Hampe, particularly when arsenic is present in rather large quantity. The filtrate from the arsenate of magnesia is acidified, and the antimony precipitated by sulphuretted hydrogen, small quantities being estimated as antimoniate of oxide of antimony (Vol. I. p. 273, 2), but larger amounts as anhydrous sulphide of antimony (Vol. I. p. 273). If tin is present also (a case of which Hampe does not take special note), the residue obtained by evaporating the sulphide of ammonium solution containing all three metallic sulphides is reoxidised with fuming nitric acid, and the antimony, arsenic, and tin separated according to Vol. I. p 487, *a*.

7. The precipitate V from 5 is dissolved in the covered funnel in warm moderately dilute nitric acid by repeatedly pouring it back; it is then washed, dried, and the filter burnt, the ash being added to the nitric acid solution; the whole is then boiled, filtered and the *silver*, if but little bismuth is present, precipitated by hydrochloric acid; the *lead* is estimated by evaporating with sulphuric acid, the copper and *bismuth* in the filtrate being finally separated by carbonate of ammonia. When larger quantities of bismuth are present, the nitric acid solution is neutralised with carbonate of soda, cyanide of potassium is added in excess, and after the precipitate containing the oxides of bismuth and lead has been filtered off, the *silver* is thrown down from the filtrate as cyanide of silver by carefully acidifying with nitric acid (Vol. I. p. 234, 3); the filtrate is then evaporated to dryness with sulphuric acid to destroy the cyanogen compounds, and the copper is precipitated in the hydrochloric acid solution as sulphide of copper. The mixture of oxides of lead and bismuth is however dissolved in hot hydrochloric acid, evaporated to a small bulk, and poured into a large quantity of water. After 24 hours, the precipitate which contains the whole of the bismuth as basic chloride of bismuth is collected, dissolved in nitric acid, and the *bismuth* precipitated by carbonate of ammonia; the whole is then boiled, the precipitate collected after standing 24 hours, and the bismuth estimated as oxide (Vol. I. p. 263, 1, a). The *lead* in the filtrate is precipitated by sulphide of ammonium and the sulphide of lead converted into sulphate of lead.

8. The bismuth estimated in 7 was that left in the residue on dissolving the copper in nitric acid; the *bismuth* which had passed into the nitric acid solution comes down along with the electrolytically deposited copper and must be determined in it. For this purpose, it is dissolved in nitric acid (for each 50 grams of copper about 350 c.c. of nitric acid of sp. gr. 1·2 are required), and the solution boiled with a large excess of hydrochloric acid in a large flask until all the nitric acid is removed. The solution after being evaporated in a porcelain basin on the water bath until the excess of hydrochloric acid is driven off and the residue has turned brown, is poured into a large quantity of boiling water, when all the bismuth separates as basic chloride, mixed with a little basic copper salt. This is collected after the lapse of 24 hours and the two metals are separated either directly or by carbonate of ammonia after repeatedly reprecipitating their hydrochloric acid solution with water.

9. The methods recommended by Hampe for estimating the *sulphur* and *total oxygen* have been already described (this vol. pp 403 and 404). Hampe has not treated of the estimation of *phosphorus* in his paper.

c. *Ascertaining the State of Combination in which the Foreign Metals occur in Coarse Copper, &c.* (Hampe*).

Formerly it was assumed that the foreign metals in rough copper were present in the metallic state; now, however, it is known that they occur partly as oxides and acids. Fleitmann† first directed attention to this circumstance, on the basis of a research by Reischauer;‡

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* Zeitschr. f. anal. Chem. 13, 188.

† Dingl. polyt. Journ. 175, 32.

‡ Dingl. polyt. Journ. 173, 195; Journ. f. prakt. Chem. 92, 508.

HAMPE,* however, made it the object of a comprehensive investigation and arrived at the methods detailed below, which rendered it possible to ascertain the condition of the foreign metals contained in rough copper, &c. The examination necessitates two sets of experiments, namely the quantitative analysis of the residue left:

1. On treating the copper with nitric acid.
2. On treating the copper with nitrate of silver.

In addition to this, the amount of oxygen must be known (that is ascertained), both the total and also that which is combined with copper as cuprous oxide in the rough copper, &c.

With regard to the basis of the analytical methods, HAMPE's original treatise must be consulted, as the details of the process are alone described here.

1. Three hundred grams of bright filed pieces of copper are treated in a 10 litre flask, with a mixture of 4 litres of water, and 2·5 litres of nitric acid of sp. gr. 1·2 at a gentle heat. When all the copper has disappeared, the whole is allowed to settle; the perfectly clear liquid is then poured off into another vessel, and the precipitate rinsed into a beaker and washed by decantation, the liquid poured off, however, being filtered through a small filter so as to prevent any loss. After washing out the contents of the filter on to the undissolved residue, the whole is boiled repeatedly with concentrated nitric acid, whereby a little more copper passes into solution; the gold in the residue is then removed by chlorine water, and any chloride of silver by repeated extraction with dilute ammonia. The residue may contain not only salts of antimonic acid but also hydrated antimonic acid, the latter originating in metallic antimony contained in the rough copper; in order to remove the hydrated antimonic acid, it must be treated with hot, rather strong, hydrochloric acid in which tartaric acid has been dissolved, until the filtrate when tested with sulphuretted hydrogen shows that antimony is no longer present. The residue thus treated and thoroughly washed is finally collected on a weighed filter which has been dried at 100°. Lastly it is shaken into a porcelain crucible as completely as possible, and the filter with the adherent particles re-weighed; in this way, the quantity used for the further analysis is ascertained. This is now fused with 3 parts of a mixture of equal quantities of carbonate of soda and sulphur, the melted mass is extracted with water, filtered, and the *antimony* together with any *arsenic* and *tin* which may be present is estimated in the solution in the manner prescribed in § 263, *b*. The residue is dissolved in nitric acid, and the silicic acid separated by evaporating and treating the residue with nitric acid; the solution is then precipitated by sulphuretted hydrogen, the precipitate collected, dissolved in nitric acid, evaporated almost to dryness with hydrochloric acid, and the solution diluted with much water. The precipitated basic chloride of bismuth is now dissolved in nitric acid, and the *bismuth* thrown down by carbonate of ammonia and estimated as oxide. The determination of the *lead*, *copper*, *nickel*, *cobalt* and *iron* is effected by the methods given in § 263, *b*.

In HAMPE's analysis of toughened copper and dry copper from Oker, about 75 per cent. of the residue insoluble in nitric acid, consisted of antimoniate of bismuth, $BiO_3,3SbO_5$, the remainder being antimoniates of lead, cuprous oxide, ferric oxide, nickel oxide and cobalt oxide. The small quantity of silicic acid found was derived apparently from the vessels. That the antimoniates existed ready formed in the copper and were not due to the action of the nitric acid, is shown by HAMPE in the varieties of copper examined by him as follows: he heated 50 grams to fusion in a current of hydrogen and dissolved the residual copper in nitric acid; it dissolved completely with the exception of traces of gold. This test must be carried out in the same way for different varieties of copper, if it is desired to know with certainty the state of combination of the foreign metals.

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* Zeitschr. f. anal. Chem. 13, 188.

2. For many metals, particularly arsenic, lead and iron, the procedure in 1 is not sufficient to determine whether they exist in the copper in the metallic state or as oxides or salts respectively. The examination in 1 may be supplemented as follows:

Eight to 10 grams of copper in the form of thin rolled sheet, or less preferably as filings (the latter must be freed from iron by a magnet and from grease by boiling in dilute potash) is covered with 100 to 150 times its weight of distilled water containing in solution rather more than sufficient *pure* neutral nitrate of silver to completely displace the copper; this is stirred round for a considerable time until no more particles of copper are visible, and the stirring is repeated at intervals during the next 24 hours. It is then collected, washed completely with the aid of the pump, dried, removed from the filter, the filter ash added, and the whole treated with nitric acid, after which it is filtered from any undissolved powder, and the silver precipitated by hydrochloric acid, avoiding any considerable excess. The liquid is then diluted, decanted, filtered, and the filtrate after being evaporated to a small bulk, is diluted and precipitated warm by sulphuretted hydrogen. In the precipitate, the *arsenic*, *antimony*, *lead*, *bismuth*, and *copper* are estimated as in § 263 b, bearing in mind the circumstance that the precipitate may still contain a little sulphide of silver.

With regard to the *antimony* found here, it should be noted that if the whole of the antimony is not contained in the copper in the form of insoluble antimoniates, some of the antimony from the antimonial compounds in the silver precipitate passes into the nitric acid solution; with reference to the copper found here, it should be noted that it originates in the cuprous oxide of the rough copper and serves for the quantitative determination of the former (see under 4). Finally, the *iron*, occurring in the copper as oxide or salts, is estimated in the filtrate from the sulphuretted hydrogen precipitate.

The examination of the liquid filtered from the silver precipitate and which contains the excess of nitrate of silver, the nitrate of copper, together with the nickel, cobalt and arsenic which existed in the copper in the reguline state, is superfluous. It may however be carried out as a check.

3. The estimation of the total oxygen is carried out as in this vol. p. 404.

4. In determining the oxygen present in the form of cuprous oxide, and also the amount of the latter,* it is necessary to ascertain

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* HAMPE (Zeitschr. f. anal. Chem. 13, 215) criticises the method given by

the reaction which takes place when cuprous oxide acts on a neutral solution of nitrate of silver. H. Rose has already made this the subject of research and shown that the copper in this connection behaves exactly as a mixture of equal equivalents of copper and cupric oxide would do, that is, produces a mixed precipitate of metallic silver and basic cupric salt. Hampe, who has carefully studied this reaction, found that the basic cupric salt has a definite composition, $4CuO,NO_5 + 3HO$, and expresses the action in the cold by the following equation:

$$3Cu_2O + 3AgO,NO_5 + xHO = \\ (4CuO,NO_5 + 3HO) + 2CuO,NO_5 + 3Ag + (x - 3)HO.$$

In accordance with this, the copper existing as cuprous oxide is found by multiplying by 1·5 the amount of copper in the silver precipitate from 2. This copper multiplied by 1·6895 gives the weight of cuprous oxide, or by 0·1895, the amount of oxygen in the latter.

5. The sulphur found in rough copper containing oxygen compounds is not in the form of sulphide, as this would react with the cuprous oxide in the molten copper, producing cuprous sulphide, and would not give rise to the evolution of sulphuretted hydrogen, which has been observed by Hampe, and previously by Abel * and Dick † on heating rosette copper in a current of hydrogen, see this vol. p. 405.

6. In order to show how the true composition of the copper may be calculated from the results obtained, the composition of a refined copper from Oker, according to Hampe's ‡ analysis and arrangement, is here given, adding where necessary, in the accompanying notes, the analytical determinations on which the results are based (see table, p. 412).

Notes to the accompanying Table.

From the residue in *c*. 1, it can be seen that the nickel cobalt and antimony are present in an oxidised condition (if the antimony is not also present as decomposable antimoniates), also that the bismuth is present as antimoniate of bismuth. From the residue obtained in *c*. 2, the amounts of nickel, cobalt, arsenic, iron and lead in an oxidised condition, are known as well as the amount of copper present as cuprous oxide.

From this we know:

1. The difference between the total amount of copper arrived at in *b*. 2 and the amount of copper present as cuprous oxide obtained in *c*. 4.
2. Estimated according to *c*. 4.
3. The difference between the total content of arsenic found in *b*. 6 and that present as arsenic acid, obtained in *c*. 1 and *c*. 2.
4. Determined according to *c*. 2.
5. The difference between the total amount of antimony found in *b*. 6 and the amount present in the form of antimonic acid obtained in *c*. 1.
6. Determined according to *c*. 1.

Aubel (Berggeist, 12, 279,—Zeitschr. f. anal. Chem. 6, 456) for determining cuprous oxide in refined or rosette copper, and gives an account (*Ibid.* p. 221) of the not universally applicable method of estimating cuprous oxide volumetrically.

* Polyt. Centralbl. 1864, 904.

† Berg- und Hüttenmännische Zeitung, 1856, p. 329.

‡ Zeitschr. f. anal. Chem. 13, 228.

Composition of No. 1 Refined Copper from Oker.

Without.			Amounts of extraneous admixture found. Reference to their state of combination.				With.			
Cu =	99·325	per cent.	as metal	99·1774 %[1]						
			,, suboxide	0·1476 %[2]	= 0·1662	per cent.	Cu_2O	containing	0·0186 %	Oxygen.
Ag =	0·072	,,	,, metal							
Au =	0·0001	,,	,, ,,							
			,, ,,	0·0467 %[3]						
As =	0·130	,,	,, acid	0·0833 %[4]	= 0·1273	,,	AsO_5	,,	0·0440 %	,,
			,, combined with BiO_3, PbO, Fe_2O_3, Cu_2O, &c.							
Sb =	0·095	,,	,, metal	0·0331 %[5]						
			,, acid	0·0619 %[6]	= 0·0822	,,	SbO_5	,,	0·0205 %	,,
Bi =	0·052	,,	,, oxide[7] partly combined with SbO_5, partly with AsO_5		= 0·058	,,	BiO_3	,,	0·006 %	,,
Pb =	0·061	,,	,, ,, [8] ,, ,, ,, SbO_5 ,, ,, AsO_5		= 0·0650	,,	PbO	,,	0·0040 %	,,
Fe =	0·063	,,	,, ,, [9] ,, ,, ,, SbO_5 ,, ,, AsO_5		= 0·090	,,	Fe_2O_3	,,	0·0270 %	,,
			,, metal[10]	0·0113 %						
Co =	0·012	,,	,, suboxide[11]	0·0007 %	= 0·0008	,,	CoO	,,	0·0001 %	,,
Ni =	0·064	,,	,, metal[12]	0·0631 %						
			,, suboxide[13]	0·0009 %	= 0·0012	,,	NiO	,,	0·0003 %	,,
S =	0·001	,,	,, sulphurous acid		= 0·0020	,,	SO_2	,,	0·0010 %	,,
							Total .	.	0·1215 %	,,
O =	0·1166	,,	of which 0·0186 % occurs in cuprous oxide							
			,, 0·0010 % ,, sulphurous acid							
Total	99·9917	,,	,, 0·0970 % ,, combined with foreign metals							

7. 8. 9. Determined according to *c.* 1 and *c.* 2, in agreement with the results from *b.* 4, *b.* 7, and *b.* 8.

10 and 12. The differences between the total amounts of cobalt and nickel found in *b.* 4, and the quantities of these metals present as oxides obtained from *c.* 1.

11 and 13. Determined as in *c.* 1.

C. Copper Alloys.

§ 264.

Of the alloys of copper, the following are here treated of : brass ; the alloy for nickel coins ; and German silver. As regards the analysis of silver-copper alloys, the reader is referred to Vol. I. pp. 235 and 463 **(143)** as well as this vol. p. 361. The alloys of tin and copper will be considered along with the tin compounds.

I. BRASS.

Brass consists of 25 to 40 per cent. of zinc, and 75 to 60 per cent. of copper. It further contains, as a rule, small amounts of lead, and sometimes very small quantities of tin and traces of iron. Its analysis can be conducted in very different ways.

First Method.

1. About 2 grams of the alloy is dissolved in nitric acid, and the solution evaporated to dryness on a water-bath ; the residue is then moistened with nitric acid, a little water added, the whole warmed, diluted still further, and any residue of stannic oxide filtered off and estimated as in Vol. I. p. 278, 1 *a*. To the filtrate, or—if tin is either not present or only in indeterminable quantity—to the solution itself, about 20 c.c. of pure dilute sulphuric acid is added, the whole evaporated to dryness on the water-bath, 50 c.c. water added and the liquid heated. If sulphate of lead remains undissolved, it is filtered off and washed with water containing sulphuric acid. The beaker containing the filtrate and washings is then removed, the dilute sulphuric acid completely displaced by alcohol and the sulphate of lead determined as in Vol. I. p. 244, 3.

2. The copper is precipitated from the sufficiently diluted filtrate by sulphocyanate of potassium, after adding aqueous sulphurous acid, and the cuprous sulphocyanate is converted into cuprous sulphide for weighing, see Vol. I. p. 258, 3. b. It should be pointed out that the ash of the filter on which the cuprous sulphocyanate is collected must be heated with full access of air for a long time in order to ensure the complete combustion of the carbonised filter ; moreover, it is best to heat the cuprous sulphocyanate in air before it is mixed with sulphur and heated to redness in a current of hydrogen.*

The solution filtered from the cuprous sulphocyanate is heated in a spacious flask, nitric acid being gradually added until the evolution of carbonic acid and nitric oxide gas produced by the decomposition of the excess of sulphocyanic acid ceases ; it is then evaporated almost to dryness, diluted, filtered if necessary, and the free acid neutralised in a flask, so as to avoid loss by spurting; the almost neutral liquid, after being heated until all the carbonic acid is driven off, is transferred to a porcelain basin and the zinc precipitated by sodic carbonate, as in Vol. I. p. 198, 1. *a*. On the one hand, the filtrate is tested by means of sulphide of ammonium, to see whether it contains any weighable amount of zinc, and on the other hand, the purity of the weighed zinc oxide is tested. For this purpose, the latter is boiled repeatedly with water, filtered into a platinum basin, the filtrate evaporated to dryness, and the slight residue of alkali salts which usually remains is heated to low redness and its weight deducted from that of the zinc oxide (provided it dissolves completely in water, otherwise it must be filtered and the clear solution again evaporated). It must then be ascertained whether the zinc oxide dissolves completely in hydrochloric acid, any residue of silicic acid being estimated when necessary; this also is deducted from the weight of the zinc oxide; finally the cold zinc chloride solution, after diluting, is supersaturated with ammonia in order to find out whether weighable traces of ferric oxide remain undissolved. If necessary, this is collected, washed, redissolved in hydrochloric acid and reprecipitated by ammonia to free the ferric hydrate from oxide of zinc.

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* See BUSSE (Zeitschr. f. anal. Chem. 17, 56).

Instead of estimating the zinc in this manner, Zimmermann's method for precipitating and weighing as zinc sulphide (see this vol. p. 417 first method) may be used.

Second Method.

The process is carried out exactly as in the first method, but the separation of the copper from the zinc is effected by sulphuretted hydrogen as in Vol. I. p. 457. It may here be pointed out that, according to G. Larsen,* the complete separation of copper from zinc can be effected by a single precipitation with sulphuretted hydrogen if the sulphide of copper has been first washed with hydrochloric acid of sp. gr. 1·05 previously saturated with sulphuretted hydrogen, and afterwards with pure sulphuretted hydrogen water.

Third Method, partly electrolytical.

About 2 grams of brass is dissolved in nitric acid, the solution evaporated, the residue dissolved in 20 c.c. of nitric acid of sp. gr. 1·2, diluted with water, and after any oxide of tin remaining undissolved has been filtered off, it is further diluted to 200 c.c., and electrolysed as described in this vol. p. 391. The copper is obtained at the negative, the lead, as peroxide, on the positive electrode; the latter is dried at 100° and weighed, see this vol. pp. 392, and 393. The solution which is now free from lead and copper, is evaporated almost to dryness, the residue taken up with water, and the zinc determined by precipitating with carbonate of soda, &c., as in the first method.

Fourth Method, entirely electrolytical.

As trustworthy processes for the separation of zinc by electrolysis are now known, the analysis of brass can also be entirely carried out electrolytically. The many different ways advocated for the electrolytic deposition of zinc show however that these methods for estimating zinc are not quite so simple and not quite so easily carried out as in the case of copper. After the copper and lead have been separated as in the third method, the electrolytic deposition of the zinc is proceeded with. The following is the method which has been found to be the best of the many proposed,* namely, that of H. REINHARDT and R. IHLE,† which only differs from that of CLASSEN and VON REIS (see note*) in that, in the former, the deposition is carried out in a solution of oxalate of zinc and potassa, and in the latter in a solution of oxalate of zinc and ammonia.

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* Zeitschr. f. anal. Chem. 17, 312.

About 2 grams of brass are taken for the analysis, and the tin (when present), copper, and lead are removed as in the third method; the nitric acid solution siphoned off from the copper and peroxide of lead is evaporated with sulphuric acid to drive off the nitric acid, then neutralised with caustic potash, and to the solution which is about 10 c.c. in volume 50 c.c. of an oxalate of potassa solution (1 : 6) and 100 c.c. of a saturated solution of sulphate of potassa are added, and the mixture submitted to the action of the current. A current sufficient to produce 90 c.c. of oxyhydrogen gas per hour is strong enough. The oxalate of zinc is broken up by the current into zinc and carbonic acid and the oxalate of potassa into potassium and carbonic acid; as potassium decomposes water, a copious evolution of hydrogen occurs at the negative pole during the experiment. The potash simultaneously produced is converted into bicarbonate by the carbonic acid given off at the positive pole. When the evolution of gas at the positive electrode ceases entirely or nearly so, and a test sample of the solution no longer gives a precipitate with sulphide of ammonium, the precipitation of the zinc is finished. As the bicarbonate of potassa formed offers a considerable resistance to the passage of the current, it is advisable to add from time to time some pure neutral sulphate of potassa to raise the conductivity of the solution. The deposited zinc is bluish white and adheres firmly to the electrode. This can be taken out at once and after being washed first in hot, then several times in cold water free from air, subsequently in alcohol, and finally in pure ether free from acid, it is dried in a desiccator (REINHARDT and IHLE) or an air bath (CLASSEN). As the zinc cannot be completely detached from the platinum without difficulty,‡ it is advisable to copper the negative platinum electrode before using it (with about 5 grams of copper). After weighing, the electrode is immersed in rather dilute, cold nitric acid. The zinc is quickly dissolved at the ordinary temperature, whilst the copper coating is only slightly attacked and keeps a perfectly bright surface, so that the electrode after washing and drying can be used again at once. If the copper coating is not perfectly bright, numerous black, loosely adherent granules appear on the zinc; these easily drop off during washing, and thus give rise to loss. With coppered electrodes, the end of the deposition of the zinc is easily known by lowering the cone further into the liquid and noting whether a light grey deposit of zinc comes down on the red surface of the copper.

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* See LUCKOW's treatise on electrometallic analysis in Dingl. polyt. Journ. vols. 177 and 178; also Zeitschr. f. anal. Chem. 19, 16; PARODI and MASCAZZINI, *ibid.* 16, 469, and 18, 587; RICHE, *ibid.* 17, 216, and 21, 119; BEILSTEIN and JAWEIN, *ibid.* 18, 588; A. CLASSEN and M. A. VON REIS, Ber. deutsch. chem. Ges. 14, 1625; Zeitschr. f. anal. Chem. 21, 255; and further "Quantitative Analyse auf electrolytischem Wege," by A. CLASSEN, J. A. MEYER, Aachen, 1882, p. 12.

† Journ. f. prakt. Chem. (N.F.) 24, 193; Zeitschr. f. anal. Chem. 21, 255.

‡ If zinc is removed from uncoppered platinum by dissolution in acids, a dark grey residue rough to the touch, is generally left behind. This is best removed by fused acid sulphate of potassa (LUCKOW).

II. NICKEL COINAGE METAL.

The so-called "nickel coins" of the German Empire consist of 75 per cent. of copper and 25 of nickel. A variation of more than 0·5 per cent. of nickel, or the presence of over 1 per cent. of foreign metals, is forbidden by law. When, as is sufficient for the determination of this legal estimation, about 1 gram of the alloy is employed for the analysis, the exact estimation of the other elements (sulphur, lead, iron, zinc, arsenic, &c.) present in small quantities must be abandoned. If these are also to be exactly determined, one of the following methods should be chosen for the chief analysis, whilst the small quantities of extraneous elements can be estimated by the methods prescribed in § 252 and § 263.

First Method.

About 1 gram of the alloy is dissolved in nitric acid; if black specks of nickel sulphide float on the surface, it is heated for a considerable time until they are dissolved, adding hydrochloric acid if necessary. The solution is then evaporated with a slight excess of sulphuric acid to drive off the nitric acid (1 c.c. of concentrated sulphuric acid is sufficient for 1 gram of the alloy), the copper precipitated as sulphocyanate (see Vol. I. p. 258 and this vol. p. 413), and the excess of sulphocyanic acid in the filtrate is decomposed by cautious heating with nitric acid; the greater part of the free nitric acid is then driven off by evaporation, and the nickel estimated as in this vol. p. 301. If during the removal of impurities in the weighed nickel, a weighable quantity of iron is found, this can be separated by a double precipitation with ammonia, and estimated. It must be observed that the hydrated ferric oxide may contain a slight amount of hydrate of alumina, derived from the potash and the vessels. See BUSSE (Zeitschr. f. anal. Chem. 17, 62).

Second Method.

The alloy is dissolved as in the first method, the copper precipitated by electrolysis (see this vol. p. 391, also p. 414 third method), and, after evaporating the excess of nitric acid in the syphoned liquid, the nickel is estimated by the first method, or electrolytically as in this vol. p. 305.

A. CLASSEN and M. A. VON REIS* employ for the electrolytic determination of nickel the clear solution of oxalate of nickel and ammonia obtained on adding an excess of oxalate of ammonia. A. CLASSEN† prescribes the following method for analysing copper-nickel alloys. The copper is precipitated electrolytically from the solution of the sulphate obtained by evaporating the nitric acid solution with sulphuric acid, the liquid siphoned off is concentrated by evaporation, neutralised with ammonia or potash, excess of oxalate of ammonia added, the mixture heated, and after adding 3 or 4 grams more of solid oxalate of ammonia is electrolysed while hot. The nickel separates rapidly as an adherent bright film.

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* Ber. deutsch. chem. Ges. 14, 1624.

† See p. 22 of CLASSEN's work referred to in this vol. p. 415.

III. German Silver (Argentan).

German silver consists of copper, zinc, and nickel in variable proportions, but sometimes containing, in addition to the slight traces of impurities there may be in these metals, a small proportion of lead and iron added intentionally, and less frequently tin. The following methods of analysis can be employed.

First Method.

About 2 grams of the alloy is dissolved in nitric acid, any tin being removed as in Vol. I. p. 478, and the lead separated by evaporating the filtrate with a slight excess of sulphuric acid (Vol. I. p. 465). The copper is then thrown down as sulphocyanate by means of sulphocyanate of ammonium (see this vol. p. 413, 2), and after the sulphurous acid has been removed by heating, the filtrate is neutralised with carbonate of soda as completely as possible; more sulphocyanate of ammonium is then added, and the zinc is precipitated with sulphuretted hydrogen by ZIMMERMANN's method (this vol. p. 276). The excess of sulphocyanic acid in the filtrate is destroyed by careful heating with nitric acid, it being better to pour the filtrate into the heated dilute nitric acid. The greater part of the excess of nitric acid is drawn off, and the nickel and any iron that may be present is determined as in this vol. p. 416 (first method).

Second Method.

The alloy is dissolved in nitric acid, any tin being removed as in the first method, and the copper and lead by electrolysis (this vol. p. 414 below). The zinc is then precipitated according to Vol. I. p. 440 (**88**), Vol. I. p. 445 (**100**) or as in the first method, and the nickel estimated in the filtrate by electrolysis (this vol. p. 416, second method), previously separating the iron if necessary. If it is also desired to precipitate the zinc by electrolysis, the zinc sulphide is dissolved in hydrochloric acid and the zinc deposited as in this vol. p. 414 (fourth method).

20. Bismuth Compounds.

§ 265.

A. Ores of Bismuth.

The ores of bismuth which occur most commonly, are native bismuth, bismuth glance, copper bismuth glance, and bismuth ochre. In analysing them, especially in the case of the first three ores, attention must be paid to the presence or probable presence of the following elements: Bismuth, lead, copper, silver, gold, antimony, arsenic, tin, iron, cobalt, nickel, zinc, sulphur and tellurium. It is therefore always advisable to make an accurate qualitative analysis before proceeding to the quantitative estimation.

In the following, an ore of the most complex constitution possible is taken, as the analytical process will meet all cases. It is evident that the analysis will be greatly simplified when only a few of the above-named elements are to be estimated, or if the amount of bismuth alone has to be ascertained.

The finely powdered ore is first dried at 100°.

1. From 2 to 5 grams is treated with pure nitric acid of 1·2 sp. gr. at first in the cold, then for a considerable time with application of heat, adding stronger nitric acid if necessary, until everything soluble is taken up; it is then diluted with water containing nitric acid. If there is an insoluble residue this is collected and washed thoroughly. The filter containing the residue is warmed with hydrochloric acid, diluted with water containing some tartaric acid, filtered, washed thoroughly with water, dried, heated to redness, and the *gangue* remaining undissolved is weighed. As this may contain gold, it is treated, after the ignition, with aqua regia, diluted, filtered, the filtrate evaporated with hydrochloric acid, and the residue tested for *gold* by ferrous chloride.

2. The hydrochloric acid solution containing tartaric acid, obtained in 1, is precipitated at 70° by sulphuretted hydrogen, and the precipitate (*a*) set aside for the present.

3. Sulphuretted hydrogen water is added to the nitric acid solution from 1, and sulphuretted hydrogen passed through it without warming. After being left for a long time, it is filtered, washed with water containing sulphuretted hydrogen, and the filter containing this precipitate (*b*) is treated—along with the precipitate *a* (from 2) which has been collected in the meantime—with warm sulphide of potassium or sodium solution. After dilution, it is filtered, the metallic sulphides of the sixth group are precipitated from the filtrate by the addition of hydrochloric acid and the precipitate (*c*) left to stand for a time.

4. The metallic sulphides of the fifth group, obtained in 3 are dissolved by heating with dilute nitric acid, filtered, the washed filter incinerated, the ash warmed with nitric acid, and this solution filtered into the one first obtained. If a slight residue is still left, this may be sulphate of lead, and should, after weighing, be tested to see if it is sulphate of lead by treating it with acetate of ammonia. Carbonate of soda is now added to the united nitric acid solutions until a permanent precipitate is just produced, then cyanide of potassium, and the whole is digested for some time at a gentle heat and filtered. The washed precipitate consisting of carbonates of lead and bismuth containing alkali, is dissolved in nitric acid and the *lead* and *bismuth* separated, according to Vol. I. p. 465 (**146**) or p. 467 (**152**).

5. The filtrate from 4, containing cyanide of potassium, must now be treated for silver, copper and small quantities of bismuth. A little sulphide of potassium or sodium is added to it, and the black precipitate produced is collected, washed, dissolved in nitric acid, and any *silver* present is precipitated by cautiously adding hydrochloric acid; the chloride of silver is collected, washed first with water containing hydrochloric acid and then with pure water, and the small quantity of *bismuth* still present in the filtrate is determined as bismuth sulphide (Vol. I. p. 264). Finally, the *copper* and possibly also *silver* in the

filtrate containing cyanide of potassium, are determined as in Vol. I. p. 466 (**148**).

6. The liquid filtered off from precipitate *b* in 3 contains the metals of the 4th group; it will also, as a rule—having been precipitated by sulphuretted hydrogen in the cold only—contain arsenic. On this account it is now evaporated to dryness with excess of sulphuric acid in order to remove the nitric acid, the residue is taken up with hydrochloric acid and water, treated at 70° with sulphuretted hydrogen, and the precipitate collected, washed, and the *iron*, *cobalt*, *nickel*, and *zinc* estimated in the filtrate. For that purpose the liquid after being concentrated, is heated with nitric acid, precipitated in the cold by an excess of ammonia, the precipitate dissolved in hydrochloric acid, and the ferric oxide thrown down as basic salt, according to Vol. I. p. 437 (**82**). The united ammoniacal solutions are rendered just acid with acetic acid, possibly after the removal by filtration of an alumina precipitate, and treated with warm sulphuretted hydrogen. If a precipitate is formed, it may contain the sulphides of *zinc*, *cobalt* and *nickel* which may be separated according to Vol. I. p. 440 (**88**) or also as in this vol. p. 354. Should the precipitate of hydrated ferric oxide obtained by the double precipitation by ammonia be pure, the *iron* may be determined simply by heating it to redness; but if it contains alumina the ferric oxide must be separated from the alumina as in Vol. I. p. 435 (**77**).

7. The precipitate *c* retained from 3 is collected on the same filter as that used in 6 for filtering the additional sulphide of arsenic thrown down; this filter, after washing, is treated with a little brominated hydrochloric acid, ammonia is added, the whole warmed, acidified with hydrochloric acid, and precipitated hot with sulphuretted hydrogen; finally the *arsenic* and *antimony*, if these alone are present, are separated as in this vol. pp. 352 and 353. If however *zinc* is also present the method described in this vol. p. 401, 4, is employed.

8. For the estimation of *sulphur* a separate portion of ore is treated as in this vol. p. 356, 1.

9. In testing for *tellurium*, and estimating it when necessary, one of the following methods may be chosen:

a. The finely powdered ore is heated moderately in a bulb tube in a current of chlorine, in the apparatus figured in Vol. I. p. 470, the volatile chlorides being collected in the receiver containing hydrochloric acid; the hydrochloric solution is then evaporated to dryness on the water bath, the residue taken up with hydrochloric acid and water, and the tellurium, now present as tellurous acid, is precipitated by a concentrated aqueous solution of sulphurous acid. If this produces a white precipitate of basic chloride of bismuth, hydrochloric acid must be added until it redissolves. If the liquid contains tellurous acid, a black precipitate of tellurium gradually forms; this is allowed to remain a few days in a warm place before filtering (H. Rose*). As the precipitate may contain bismuth, it is dissolved in hypochlorite of soda with addition of hydrochloric acid, evaporated, thrown down again by sulphurous acid as above, and the tellurium weighed after washing quickly and drying at 100°.

b. The finely ground ore is intimately mixed with three times its weight of carbonised cream of tartar, and exposed to a moderate red heat for an hour in a luted crucible; this converts any tellurium into telluride of potassium. The cooled mass is ground up, transferred to a filter and washed thoroughly with water free from air and which has previously been boiled and allowed to cool. If tellurium is present, the washings are red and on exposure to air gradually deposit tellurium as a grey powder (Wöhler*).

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* His "Handbuch der analyt. Chem." 6th ed. R. Finkener, vol. ii. p. 439.

B. Bismuth Alloys.

Wood's metal, consisting of tin, lead, bismuth and cadmium, may be taken as an example of these:

1. The weighed sample is treated with nitric acid of sp. gr. 1·2 until it ceases to have any action, the whole evaporated to dryness on a water bath, and the residue warmed with nitric acid and water; the impure hydrated metastannic acid (containing oxides of lead and bismuth) is filtered off, heated to redness and weighed. It is then fused with carbonate of soda and sulphur, or with liver of sulphur, excluding the air (Vol. I. p. 475, β); the product is treated with water, the sulphides of lead and bismuth which remain undissolved are filtered off, and the residue, after washing, is dissolved in hot dilute nitric acid. Should oxide of tin still remain undissolved, the fusion with alkali sulphide must be repeated, &c. The portions of *lead* and *bismuth* which have passed into the nitric acid solution are separated and estimated as in Vol. I. p. 465 (**146**), the weight of oxide is deducted from that of the impure stannic oxide and in this way the amount of the pure *stannic oxide* is obtained.

2. In the nitric acid solution filtered from the hydrated metastannic acid, the greater part of the *lead* and *bismuth* contained in it are separated from each other and from the *cadmium* according to Vol. I. p. 467 (**152**), or the lead is removed as sulphate (Vol. I. p. 465 [**146**]), the bismuth precipitated as basic chloride (Vol. I. p. 265, 4), and the cadmium estimated in the evaporated filtrate as in Vol. I. p. 266, 1 or 2.

Instead of converting the basic chloride of bismuth into the metal by fusing it with cyanide of potassium, this can be accomplished electrolytically. According to Classen and v. Reis† the basic chloride of bismuth must, for this purpose, be dissolved in hydrochloric acid, the solution evaporated with excess of sulphuric acid, taken up with water, oxalate of ammonia added in excess, and the mixture electrolysed. The platinum basin which serves as the negative electrode (this vol. p. 389) must be filled to the brim in order to secure as large a depositing surface as possible. A separation of peroxide of bismuth (see also Luckow‡) is generally observed at the positive electrode, but this slowly disappears again. To preserve the reduced metal from oxidation, the last traces of water must be removed by copious washings with alcohol and ether free from water.

The cadmium may also be electrolytically deposited from the liquid filtered from the basic chloride of bismuth. The free hydrochloric acid is removed by evaporation, excess of oxalate of ammonia is added, and the whole electrolysed. The cadmium separates as a grey, not very adherent, film and care must therefore be exercised during washing (CLASSEN and REIS *).

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* His "Die Mineral-Analyse in Beispielen," 2nd ed. p. 109.

† Ber. deutsch. chem. Ges. 14, 1626; Zeitschr. f. anal. Chem. 21, 256; Classen's "Quant. Anal. auf elektrolyt. Wege," p. 18.

‡ Zeitschr. f. anal. Chem. 19, 16.

C. Bismuth Salts.

The basic nitrate (magistery of bismuth, bismuth white) will serve as an example, this being often subjected to analysis on account not only of its containing impurities, but also of the adulterations with barytes, talc, &c., of which it is the object, and of the intentional admixture of basic chloride of bismuth met with in the commercial product.

I. Complete Analysis.

In addition to the normal constituents, that is oxide of bismuth, nitric acid, and water, the substances to be considered in a complete analysis are, of the bases: oxide of zinc, ferric oxide, oxide of lead, lime, and magnesia; and of acids: arsenic acid, hydrochloric acid, sulphuric acid, and carbonic acid. Finally, adulterants insoluble in nitric acid may also be present.

1. A sample is dried at 100°, and the *water* which is given off at this temperature is determined (according to PHILLIPS and MENIGAUD the whole of the water comes off at 100°, but L. GMELIN says that about 3 per cent. remains behind).†

2. If the amount of *water* still remaining in the substance after drying at 100° is to be directly estimated, a weighed portion is heated to redness in a glass tube in a slow current of dry carbonic acid gas, and the vapours are passed first over red hot copper turnings, and then into a weighed chloride of calcium tube (this vol. p. 36).

3. From 1 to 2 grams of the substance dried at 100° is treated with about 8 times the amount of cold nitric acid of sp. gr. 1·2. If *carbonic acid* is evolved, this must be determined in a separate portion, and if there is any *insoluble residue* this indicates the presence of one of the adulterants already mentioned; in such case this must be filtered off, washed first with water containing nitric acid, then with pure water, heated to redness and weighed.

4. Sulphuretted hydrogen water is added to the nitric solution from 3, and sulphuretted hydrogen gas is passed into the cold liquid; this is filtered after settling. The washed precipitate (*a*), after being treated with sulphide of ammonium, warming gently, is diluted, filtered, washed thoroughly, the black precipitate, dissolved in warm dilute nitric acid, and the *lead* and *bismuth* separated as in Vol. I. p. 465 (**146**). Hydrochloric acid in slight excess, however, is added to the sulphide of ammonium filtrate, and the precipitate of arsenic sulphide (*b*) which will probably be produced is reserved meanwhile.

5. The solution filtered from the precipitate *a* in 4, after being evaporated to dryness along with a slight excess of sulphuric acid in order to drive off the nitric acid, is diluted, precipitated at 70° with sulphuretted hydrogen, and if any precipitate (*c*) is formed, this is collected, washed, and transferred to the filter which contains the

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* Ber. deutsch. chem. Ges. 14, 1628; CLASSEN "Quant. Anal. auf elektrolyt. Wege," p. 23.

† L. GMELIN, Handb. der Chem. 4th ed. vol. ii. p. 858.

precipitate *b* from 4. The contents of the filter are dissolved in caustic potash and the *arsenic* contained therein is determined as in this vol. p. 352, *b*.

6. *Iron* and *zinc* are precipitated on adding sulphide of ammonium to the filtrate from the precipitate *c* (or the clear solution if there was no precipitate), the *lime* and *magnesia* being determined in the filtrate. The former are separated according to § 160, and the alkaline earths by the method given in § 154.

7. If the presence of chlorine or sulphuric acid has been indicated in the qualitative examination, a fresh portion is fused with a fourfold quantity of carbonate of potassa and soda; the product is then treated with water, filtered, washed with hot water containing a little carbonate of soda, the filtrate made up to a fixed volume, and the *chlorine* estimated in one half (Vol. I. p. 354), and the *sulphuric acid* in the other (Vol. I. p. 299).

8. The content of *nitric acid* is as a rule ascertainable by deducting the amount of water found in 2 from the loss which occurs when the substance, dried at 100°, has been heated to redness. Should this method not be available from any cause, one or other of the methods given in § 149 must be employed for estimating the nitric acid.

II. Buisson and Ferray's* estimation of the bismuth present as basic nitrate in bismuth white.

This is a volumetric method and is based on the precipitation of bismuth from an acetic solution by means of iodic acid. The white precipitate of iodate of bismuth thus produced is insoluble in water and dilute acids, acetic acid in particular does not dissolve a trace of it.

The solutions required are: a solution of iodic acid containing 30 grams of crystallised iodic acid per litre; a saturated solution of pure iodide of potassium; and a solution of hyposulphite of soda, the latter being of such a strength that 30 to 40 c.c. will be required to convert into hydriodic acid the iodine liberated from iodide of potassium by 10 c.c. of the iodic acid solution. The solution of hyposulphite of soda is first standardised relatively to the iodic acid solution by adding to 10 c.c. of the latter dilute sulphuric acid and iodide of potassium in sufficient excess, and ascertaining how much of the hyposulphite of soda solution is required to destroy the iodine coloration, or if starch paste is used the iodide of starch coloration (see Vol. I. p. 371). The titre of the iodic acid solution is then determined, and for this purpose about 0·3 gram of pure bismuth, or 0·4 gram of pure oxide of bismuth is dissolved in nitric acid and the solution diluted somewhat with water; bicarbonate of soda is then added until a slight permanent precipitate appears, which is redissolved by acetic acid in sufficient excess to prevent a subsequent partial precipitation by water, and is poured into a 250 c.c. measuring flask, containing 25 c.c. of the iodic acid solution; this is then filled with water up to the mark, mixed, allowed to settle and filtered through a dry filter. Dilute sulphuric acid is now added to 100 c.c. of the clear filtrate, then as much iodide of potassium solution as is needed to dissolve all the iodine liberated,† finally hyposulphite of soda until

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* Moniteur scientifique [iii.], 3, 900; Zeitschr. f. analyt. Chem. 13, 61.

† This reaction is represented by the equation—

$$IO_5 + 5KI + 5(HO,SO_3) = 5(KO,SO_3) + 6I + 5HO.$$

the iodine (or iodide of starch) coloration disappears. By the last titration, the amount of iodic acid still remaining in solution is ascertained, and from the difference, the volume of iodic acid solution required to precipitate the bismuth.

To test the bismuth white, about 0·5 gram is dissolved in a few drops of nitric acid and the process carried out as described above, boiling however after adding the acetic acid. If there is any insoluble residue—basic chloride of bismuth or basic ferric salts—the whole is filtered into the 250 c.c. flask, and the process carried out in the manner already described for standardising the iodic acid solution. The amount of bismuth, present as basic nitrate, is calculated from the iodic acid required for precipitation.

21. ANTIMONY COMPOUNDS.

§ 266.

A. Antimony Ores.

Of the ores of antimony, the most widely distributed and important, namely antimony glance (stibnite), will serve as an example. In it are found, besides antimony and sulphur, usually lead, iron and arsenic, occasionally also copper, and frequently gangue insoluble in acids.

I. Complete Analysis.

If the proportion of lead is high, the powdered ore dried at 100° is decomposed by heating in a current of chlorine; otherwise the process is exactly as for fahlerz (this vol. p. 384). If, on the other hand, but little lead is present, the following method of treatment in the wet way is satisfactory.

1. About 2·5 grams of the finely powdered ore, dried at 100°, is placed in a flask, three or four times the amount of chlorate of potassa is added and then, without warming, hydrochloric acid of sp. gr. 1·12 (not stronger as slight explosions would result); the liquid becomes yellow and the ore gradually dissolves. After prolonged action in the cold, the mixture is heated moderately on the water bath until all the ore has disappeared. A concentrated solution of tartaric acid is now added and the whole diluted with water. Usually a little *gangue* and frequently also a little sulphur remain unoxidised. The liquid is passed through a filter which has been dried and weighed at 100° into a 250 c.c. flask; the filter is washed thoroughly, dried at 100°, weighed, heated to redness, and re-weighed. In this way both the weight of the gangue and that of the *sulphur* remaining undissolved are ascertained.

2. The solution in 1 is diluted up to the mark, mixed, 100 c.c. measured off, diluted, and sulphuretted hydrogen passed in at 70°. After settling, it is filtered, and in the filtrate any *iron* and other heavy metals, earths, or alkaline earths which may be present are determined. The precipitate however, after washing, is treated with sulphide of potassium or sodium solution at a gentle heat until all the sulphide of antimony has dissolved; it is then diluted, filtered, the residue washed thoroughly, and the filtrate precipitated with hydrochloric acid; the washed precipitate is dissolved in caustic potash, chlorine passed in, and the *antimony* and *arsenic* estimated as in this vol. pp. 352 and 353.

3. The residual undissolved sulphide of lead from 2, which may also contain an admixture of sulphide of copper is dissolved in hot dilute nitric acid, and the *lead* and *copper* separated according to Vol. I. p. 465 (**146**).

4. 100 c.c. of the solution obtained in 1—after the excess of acid has been partially neutralised with ammonia—is precipitated by chloride of barium, and the sulphate of baryta, after being heated to low redness with access of air, is treated with very dilute hydrochloric acid to extract any carbonate of barium which may have been formed by the ignition of admixed tartrate of barium; the residue is then washed thoroughly, heated to redness and weighed. The main portion of the *sulphur*, which became dissolved as sulphuric acid during the treatment of the ore with hydrochloric acid and chlorate of potassa is thus determined.

II. Method for determining the Antimony only.

First Method.

This is based on the fusion of the finely powdered ore with carbonate of soda and sulphur (recently again recommended by F. Becker[*]), with previously carefully dehydrated hyposulphite of soda (recommended by A. Froehde[†] and lately by E. Donath,[‡] for the decomposition of antimony ores) or with liver of sulphur (sulphide of potassium); the fusion is effected in a covered porcelain crucible. The fused mass, on extraction with water, yields a yellow solution containing all the antimony and arsenic as sulphur salts. These are precipitated by hydrochloric acid, collected, and the precipitate washed very thoroughly; the funnel is then closed below and filled with a solution of carbonate of ammonia which after being allowed to remain 12 hours is drawn off, carrying with it the arsenic sulphide in solution. The residue on the filter is washed with water containing carbonate of ammonia and the antimony determined either as antimoniate of oxide of antimony (Vol. I. p. 273[§]) or preferably as sulphide of antimony (Vol. I. p. 272). In the latter case, the precipitate must be collected on a filter dried at 100°, and after washing with carbonate of ammonia the filter and precipitate are dried at 100°, and weighed, so that an aliquot part of it may be heated in a current of carbonic acid.

Second Method (by F. Weil[‖]).

Although this method to a certain extent follows from what has been already stated in this vol. p. 395, it will be useful to briefly repeat the procedure here. The normal chloride of copper solution mentioned in the reference and the stannous chloride solution standardised accordingly, are both required.

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[*] Zeitschr. f. anal. Chem. 17, 185.

[†] Poggendorff's Annal. 119, 317; Zeitschr. f. anal. Chem. 2, 362.

[‡] Zeitschr. f. anal. Chem. 19, 23.

[§] From Bunsen's later work on the estimation of antimony (Ann. d. Chem. u. Pharm. 192, 305; Zeitschr. f. anal. Chem. 18, 267), it appears that the method he previously recommended for the determination of antimony by converting the sulphide into antimoniate of oxide of antimony (see Vol. I. p. 273) is not adapted for accurate estimations, as the temperature at which the antimonic acid is converted into antimoniate of oxide of antimony and that at which the latter is resolved into oxide of antimony and oxygen, are very close together, consequently the weights obtained vary with the temperature employed and the duration of the ignition.

[‖] "Procédés Fr. Weil pour le dosage volumétrique du cuivre, du fer, et de l'antimoine" (printed as MS.).

About 2 to 5 grams of the ore is dissolved in a large amount of hydrochloric acid with the addition of a small quantity of chlorate of potassa, permanganate of potassium is added until the red tinge is permanent, and the solution is then boiled until it disappears again and the vapours no longer turn iodide of potassium starch paper blue. The liquid is now diluted to 250 c.c. with an aqueous 5 to 10 per cent. solution of tartaric acid, mixed, and 10 c.c. placed in a small porcelain basin; 10 c.c. of the normal chloride of copper solution is added, and the liquid evaporated to about half; 25 c.c. of hydrochloric acid is added, and then stannous chloride solution from the burette until the solution is decolorised. By deducting from the volume used, the amount corresponding with the chloride of copper solution, the difference is what has served for reducing the pentachloride of antimony to trichloride, and from this the antimony can be estimated according to the equation in this vol. p. 396.

Third Method (by Tamm*).

This is founded on the fact that antimony when present as trichloride in a concentrated, but only slightly acid solution, can be completely precipitated by gallic acid as gallate of antimony, whilst other metals are not precipitated under these conditions.

About 1 gram of the ore is dissolved in hydrochloric acid with addition of a small quantity of chlorate of potassa, and after the free chlorine has been expelled from the solution by gently warming, iodide of potassium is added to reduce the pentachloride of antimony to trichloride; it is then heated to drive off the liberated iodine, the solution being brought to the necessary degree of concentration at the same time. According to Tamm, the presence of chloride of potassium prevents loss of antimony by volatilisation. A moderate excess of a concentrated freshly prepared gallic acid solution is now added, and the whole allowed to settle. The presence of gallic acid in excess is easily recognised by taking a drop of the liquid from above the precipitate, putting it on a filter paper and adding a drop of ammonia, and noting whether a reddish coloration is produced. The white precipitate of gallate of antimony can *not* be washed on a filter. The washing must be effected by decantation, three or four times repeated, using hot water, and pouring the liquid through a double filter, finally bringing the precipitate on to the same filter, where it is washed again once or twice. If dried at 100° it has, according to Tamm, the composition, $SbO_3,C_{14}H_5O_9$; it has a strong attraction for water and contains 40·85 per cent. of antimony;† if dried at 80° it contains 2 equiv. of water more, and only 38·77 per cent. antimony.‡ The gallate of antimony can of course be dissolved in hydrochloric acid, tartaric acid added, the mixture diluted, precipitated by sulphuretted hydrogen, and the antimony estimated as sulphide of antimony. If the other metals are also to be estimated, they must be thrown down, from the liquid containing the excess of gallic acid, by means of sulphuretted hydrogen and sulphide of ammonium respectively.

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* Chem. News, 24, 207 and 221; Zeitschr. f. anal. Chem. 14, 351.

† The formula corresponds with (Sb = 122) 39·74 per cent.

‡ The formula corresponds with (Sb = 122) 37·54 per cent.

Fourth (Electrolytical) Method.

Parodi and Mascazzini,* Luckow,† and Classen and v. Reis ‡ have studied the electrolytic deposition of antimony. The deposition of this as an adherent coating on the electrode, is best accomplished in a solution of an antimonial sulphur salt. For this purpose, the antimony ore is dissolved in hydrochloric acid with addition of chlorate of potassa, and after adding tartaric acid the solution is diluted and precipitated by sulphuretted hydrogen in the cold; the precipitate is then washed with water, treated with a solution of carbonate of ammonia to remove any precipitated sulphide of arsenic, and washed. It is now only necessary to treat the precipitate with a solution of yellow sulphide of potassium or sulphide of sodium at a gentle heat, filter off the undissolved sulphides of the metals of the fifth group, and at once precipitate the antimony from the solution of its sulphur salt by electrolysis. The electrode carrying the deposit, after being washed with water, spirit of wine, and ether, is dried and weighed.

B. Alloys of Antimony.

Type metal, the most important of the alloys of antimony, may be taken as an example of this class; it is made of lead and antimony only, or of lead, antimony, and tin, occasionally accompanied by a small amount of copper.

The finely divided alloy is treated with nitric acid, adding some tartaric acid, then mixed with ammonia in slight excess followed by excess of yellow sulphide of ammonium and digested in a closed flask until it is certain that all the sulphide of antimony and stannic sulphide are dissolved. The sulphide of lead, which may contain some sulphide of copper, is collected, washed, and the estimation of the lead or separation of the lead and copper carried out, as in Vol. I. p. 244, Vol. I. p. 465, or this vol. p. 414 (third method).

When antimony alone is present in the filtrate, it may be at once deposited electrolytically (see above). It can also be thrown down from the filtrate by hydrochloric acid, and the antimony estimated as black sulphide of antimony as in Vol. I. p. 272. If tin is present along with the antimony, proceed as in this vol. p. 401, 4. C. Winkler's method of separating antimony from tin will be described in § 267.

22. COMPOUNDS OF TIN.

§ 267.

A. Tin Ores.

Of the ores of tin, only the two most important, tinstone and tin pyrites will be considered here. In analysing the former, it must be borne in mind that stannic oxide is frequently accompanied by ferric oxide, oxide of manganese, alumina and silicic acid. In many tinstones, oxide of lead, tantalic acid, tungstic acid, and small quantities of silver are present. On the other hand, tin pyrites always contains, besides tin and sulphur, copper, iron and zinc, and, moreover, is frequently accompanied by gangue.

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* Zeitschr. f. anal. Chem. 18, 587.

† *Ibid.* 19, 13.

‡ Ber. deutsch. chem. Gesell. 14, 1629; Zeitschr. f. anal. Chem. 21, 257; Classen's "Quant. Anal. auf elektrolyt. Wege," pp. 15 and 42.

1. Tinstone.

As tinstone is insoluble in acids, the first step in its analysis is to effect disintegration. This is accomplished by fusing it with hydrate of potassa or soda in a silver crucible, or by the aid of liver of sulphur, the latter being preferable.

1. The tinstone must be in an extremely fine state of division. According to H. Rose,* it should be mixed with 3 parts of carbonate of soda and 3 parts of sulphur, and fused in a well-closed porcelain crucible; the disintegration may be effected by the aid of ready prepared liver of sulphur in place of the above mixture. When cold, the mass is treated with water, and the black residue, separated from the yellow solution by filtration, is washed with water containing sulphide of ammonium.

2. The residue from 1 is treated with hot, somewhat diluted, nitric acid. If any residue of unattacked tinstone still remains, it must be filtered off, re-fused with sulphide of potassium after being heated to redness, and the mass again treated as above. The constituents of the nitric acid solution ascertained by qualitative analysis as belonging to the 5th, 4th and 3rd groups are removed by the methods prescribed in § 160–164. Any residue insoluble in nitric acid, remaining after the second fusion, may be tantalic acid and gangue; this should be fused with acid sulphate of potassa, treated with water, and tested for the presence of *alumina* by ammonia. After the insoluble residue has been re-weighed, it is treated with hydrofluoric acid and sulphuric acid. If any residue remains, it is to be regarded as *tantalic acid*, but of course further tested. The *silicic acid* is estimated by the difference.

3. The solution of tin sulphur salt obtained in 1, and possibly in 2, is precipitated by hydrochloric acid, allowed to settle, and the sulphide of tin, after being filtered off and washed, is dissolved in hydrochloric acid containing bromine, the solution precipitated by nitrate of ammonia and the tin estimated as *stannic oxide*, according to Vol. I., p. 279 *b*. If the tinstone contains *tungstic acid*, the larger part of the tungsten is found along with the sulphide of tin. A separation of the two metals must then be made by one of the methods given in this vol. p. 428.

4. As silicic and tungstic acids may be present in the liquid filtered from the sulphide of tin, for tungsten is not completely precipitated as sulphide by acids from solutions of its alkali sulphur-salts, the solution is evaporated to dryness, the residue heated to 120°, again treated with hydrochloric acid and water, and evaporated once more to dryness, these operations being repeated several times. If the residue is now treated with hydrochloric acid and water, all the tungstic acid remains behind (H. Rose), and also the silicic acid when present. The insoluble residue is collected, washed with dilute hydrochloric acid, heated to

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* "Handbuch der Analyt. Chemie," by H. Rose. 6th ed., R. Finkener, vol. ii. p. 275.

redness, and weighed; the *tungstic acid* is then separated from the silicic acid by fusing with acid sulphate of potassa and treating the mass with water, the *silicic acid* remaining undissolved.

2. Tin Pyrites.

1. From 2 to 3 grams of the finely powdered mineral dried at 100° is treated with hydrochloric acid with the addition of chlorate of potassa, or else with aqua regia, until the tin pyrites is completely decomposed; it is then diluted, heated in order to drive off the free chlorine, filtered into a 250 c.c. flask through a filter which has been dried at 60°, and the sulphur and gangue contained in the residue, after being dried at 60° and weighed, is separated by heating the mixture to drive off the sulphur.

2. The solution is made up to 250 c.c., mixed, and the sulphur dissolved in it as sulphuric acid is determined in 100 c.c. by neutralising the greater part of the free acid with ammonia, adding chloride of barium and estimating the sulphate of baryta. As this may contain stannic oxide, either the sulphuric acid in it is determined as in Vol. I. p. 303 *b a*, or after heating to redness, it may be boiled with a solution of carbonate of soda which is frequently renewed so as to completely decompose the baryta salt. As soon as the liquid filtered off no longer contains sulphuric acid the precipitate is washed and the carbonate of baryta dissolved in dilute nitric acid. Any stannic oxide it may contain remains undissolved; this must then be washed, heated to redness, weighed, and deducted from the weight of the impure sulphate of baryta.

3. Another 100 c.c. of the pyrites solution in 2 is employed for the estimation of the metals. For that purpose, it is precipitated with sulphuretted hydrogen at a gentle heat, and the copper and tin in the washed precipitate are separated by sulphide of potassium, as in Vol. I. p. 474 (**167**), and the iron and zinc in the filtrate as in Vol. I. p. 437 (**82**).

B. Varieties of Tin.

Tin is met with in commerce in somewhat varying degrees of purity. The purest kinds such as Banca tin, contain 99·90 to 99·96 per cent. of tin, whilst frequently only 94 per cent. of tin are found in crude tin. The foreign elements which should be considered in analysing varieties of tin are more particularly the following: lead, copper, bismuth, antimony, arsenic, tungsten, molybdenum, iron, zinc, manganese, nickel, chromium, and sulphur. As, in order to estimate the very slight quantities of foreign metals present, it is necessary to work with considerable quantities of tin, a complete analysis of tin is no easy task. If it is only a question of estimating the foreign metals present in larger quantity, such as *copper*, *lead*, and *iron*, the following method answers satisfactorily.

About 3 grams of the finely divided tin is treated with nitric acid until all the tin is oxidised, the whole evaporated to dryness in a large porcelain crucible, and then fused with about 10 grams of liver of sulphur, excluding the air as completely as possible. The cold mass is then treated with water at a moderate heat, and in this way the tin (together with any antimony and arsenic) passes into solution as sulphur-salt, whilst the metals of the fifth and fourth groups remain undissolved. The analysis is then conducted as prescribed for tinstone (this vol. p. 427).

If a tin contains *tungsten*, this also passes into the sulphide solution, and on precipitating the latter with dilute sulphuric acid (which is preferable to hydrochloric acid when the tin sulphide has to be directly converted into stannic oxide) tin sulphide is obtained containing sulphide of tungsten. If the sulphides are converted into oxides by moistening them with nitric acid and heating to redness, the tin may be completely volatilised as chloride by heating the residue repeatedly with chloride of ammonium, the tungstic acid remaining behind (H. Rose*). According to Talbot,† the separation of the stannic oxide from the tungstic acid may also be effected by fusing the oxides with five parts of cyanide of potassium and treating the mass with water. The tin remains behind in the metallic state whilst tungstate of potassium passes into solution. The tungstic acid in this can be most simply estimated by the method above described (this vol. p. 427).

The method of estimating small quantities of *antimony* and *arsenic* in metallic tin has been already described in Vol. I. p. 492, *c* and *d*. As regards the separation of the precipitated arsenic and antimony see also this vol. pp. 352 and 353.

If it is desired to estimate, in metallic tin, small quantities of metals whose chlorides are either not volatile or only volatile at relatively high temperatures, this can be effected by heating the tin to fusion in a current of chlorine, either in a retort or distributed in porcelain boats in a tube. The tin, together with the antimony, arsenic, &c., volatilise as chlorides and may be collected in a cooled receiver, whilst the chlorine compounds of copper, lead, &c., remain behind (Vol. I. p. 469, and this vol. p. 384 *b*).

The amount of *stannous oxide*, and also the *tungsten* and *molybdenum* in metallic tin can be determined, according to Balling ‡ by pouring about 1 litre of a solution of ferric chloride (containing 20 grams of iron per litre), free from acid and warmed to 30°, on to 10 to 20 grams of the finely divided metal, and digesting the mixture with occasional stirring, and the addition of more ferric chloride if necessary, sufficiently long (about 24 hours) to dissolve all the tin as protochloride. The undissolved residue consisting of dark, fine granules of stannous oxide, which may be mixed with whitish flakes of hydrated tungstic and molybdic acids, as well as oxide of antimony, and—in the case of tin rich in lead—also of lead, is then filtered off. If this residue is free from other metals, it is washed, converted into stannic oxide by heating it to redness with free access of air, and weighed. Should it contain lead, a separation must be effected (see Vol. I. p. 475, β.); whilst if it contains tungstic or molybdic acid, Balling recommends treating the undissolved stannous oxide with aqueous ammonia. The acids named then dissolve, whilst the stannous oxide (and any oxide of antimony which may be present) is left behind. On evaporating the ammoniacal solution in a porcelain crucible and moderately heating the residue, the tungstic and molybdic acids remain behind, and can be weighed.

The following method of separation may be employed (according to H. Rose §): Tartaric acid is added to the ammoniacal solution of the acids, then hydrochloric acid, and the *molybdenum* thrown down from the solution by long-continued treatment with sulphuretted hydrogen

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[*] See his "Handbuch der analyt. Chem.," 6th edition by Finkener, p. 352.

[†] Zeitschr. f. anal. Chem. 10, 343.

[‡] Oesterr. Zeits. f. Berg- und Huttenwesen, 1878, p. 169.

[§] "Handbuch der analyt. Chem.," by H. Rose, 6th ed. by Finkener, vol. ii. p. 358.

at a moderate heat; the liquid is filtered, evaporated to dryness, the residue heated to redness with free access of air until all the carbon is consumed, adding nitrate of ammonia if necessary, and the residual *tungstic acid* is weighed. If it is only necessary to separate the stannic oxide from tungstic acid, the mixture may be repeatedly heated to redness with chloride of ammonium until all the tin is volatilised as chloride, or TALBOTT's method of separation (this vol. p. 429) may be employed.

If the tin contains *sulphur*, this is determined by dissolving the tin by heating it with hydrochloric acid, and estimating the sulphuretted hydrogen in the evolved hydrogen according to one of the methods given for the determination of sulphur in cast iron (this vol. p. 330).

C. Alloys of Tin.

One of the alloys of tin, namely, Wood's metal, has already been treated of (this vol. p. 420). The analysis of some others will here be considered.

I. Alloys which consist principally of Copper and Tin (Antique bronze, Patent bronze, Bell metal, Speculum metal, bronze for Medals and Coins, Phosphor-bronze, &c.)

The above-named important alloys contain tin and copper in varying proportions, but other elements are found in them, either as the result of impurities in the alloyed metals, or as being purposely added in order to give special properties to the bronze.

In making the analysis, particular attention must be paid to the following elements, in addition to copper and tin—namely, lead, silver, bismuth, antimony, arsenic, iron, cobalt, nickel, and zinc; sometimes the alloys contain small quantities of sulphur. Phosphor-bronze contains phosphorus as an important constituent.

For the analysis of bronzes several different methods may be employed.

First Method.

1. About 2 to 5 grams of the finely divided alloy is treated with nitric acid as in Vol. I. p. 278, 1. The mass, evaporated nearly to dryness, is treated with water, and the solution filtered off from the undissolved hydrated metastannic acid. BUSSE,* in the case of analyses of bronze coins (an alloy poor in tin), recommends pouring 6 c.c. of nitric acid of 1·5 sp. gr. on to 1 gram of the alloy in the form of cuttings, in a glass beaker, followed by the gradual addition of 3 c.c. of water, the vessel being quickly covered up. As the water mixes with the acid, dissolution takes place; when this is completed, the mixture is heated to boiling, 50 c.c. of boiling water is added, and the whole allowed to settle and filtered.

If the alloy has been treated with nitric acid in one or other of these ways, or by BRUNNER's method, as in Vol. I. p. 478, the stannic oxide which is obtained on thoroughly washing, heating to redness, and weighing the undissolved hydrated metastannic acid, must be further tested, as it may contain oxide of lead, oxide of copper, ferric peroxide, and other

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* Zeitschr. f. anal. Chem. 17, 64.

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oxides of the fourth and fifth groups, as well as arsenic acid, phosphoric acid, and silicic acid. It is therefore powdered, and an aliquot part fused with liver of sulphur as described in Vol. I. p. 475, β., in order to determine, in any residue remaining after treatment with water, the oxides of lead, copper, iron, &c., adhering to the stannic oxide, their weight being subtracted from the impure stannic oxide. A second aliquot part is tested for silicic acid by Khittel's method (Vol. I. p. 478). If the bronze contains weighable quantities of arsenic and antimony, the portions of these carried down along with the stannic oxide will be found in the solution of the sulphur salts. In that case this solution must be precipitated by dilute hydrochloric acid, and the tin separated from the arsenic and antimony (this vol. p. 401, 4).

If the bronze contains phosphorus it is all found as phosphoric acid along with the stannic oxide (see Vol. I. pp. 309 and 310). The quantity of it as ascertained in 3, must therefore be deducted from the weight of the impure stannic oxide.

2. If the nitric solution contains all the metals already alluded to, as occurring in bronzes, their separation must be effected in the manner set forth for copper (this vol. p. 400, *a*). If, however, as is usually the case, only copper, lead, iron and zinc are to be estimated in the solution, the process is the same as that for brass (this vol. p. 413).

3. When a bronze contains phosphorus, it is dissolved by treating it with nitric acid as described in 1, and then after driving off the greater part of the nitric acid by evaporation, the residue is moistened with fuming hydrochloric acid and left in contact with it at the ordinary temperature or slightly warmed, stirring repeatedly; water is now added, in which, if the operation has been properly carried out, everything will dissolve. The metals of the fifth and sixth groups are thrown down by sulphuretted hydrogen at a moderate heat, filtered, washed, the filtrate evaporated repeatedly with nitric acid, the phosphoric acid produced from the phosphorus is precipitated by molybdenum solution, and the estimation of it carried out as in Vol. I. p. 307 β.

4. If the bronze contains small quantities of sulphur this is determined as in the third method.

Second Method.

The alloy is dissolved as in Vol. I. p. 479, and the tin precipitated either by Löwenthal's method, using nitrate of ammonia, or according to Rose's method by means of dilute sulphuric acid, diluting largely (Vol. I. p. 279). The other metals are found in the filtrate, either entirely, or nearly so. Of course the weighed stannic oxide obtained in this way must be further tested as directed in 1 of the first method.

Third Method.

1. The finely divided alloy is treated in a current of chlorine at a gentle heat, as in Vol. I. p. 480–8 and this vol. p. 384; a separation being effected, on the one hand of the volatile chlorine compounds of tin, antimony, arsenic, bismuth, &c., which collect in the receiver, and on the other of the residue of non-volatile or slightly volatile chlorine compounds of copper, lead, &c., as in Vol. I. section V.

2. The treatment of the alloy in a current of chlorine is also

adapted to the estimation of small quantities of sulphur in bronze; the contents of the receiver then contain the sulphur as sulphuric acid. All the precautions mentioned in this vol. p. 403 must be taken, and as the sulphate of baryta obtained may easily contain stannic oxide, the sulphuric acid therein must be estimated according to Vol. I. p. 303 *b. a.*

Fourth Method, by CLASSEN,* *based on the electrolytic deposition of the tin, presupposing the presence of copper and tin only, or of copper, tin, phosphorus, and zinc.*

1. The alloy is treated with nitric acid as in the first method, the hydrated metastannic acid is filtered off, washed, digested with strong hydrochloric acid, the greater part of the latter evaporated, and water added so as to obtain a solution of the metastannic chloride. From this solution, the *tin* is thrown down electrolytically, which can be done without difficulty, and then washed without interrupting the current. The liquid removed from the deposited tin is evaporated repeatedly with nitric acid, united with the nitric solution first obtained, and the *copper* determined therein (this vol. p. 385, 2).

2. If the bronze contains *phosphorus*, the whole of it is found as phosphoric acid in the liquid separated from the electrolytically deposited tin. This is added to the nitric solution first obtained, and containing the main portion of the copper, the free acids are evaporated on the water bath, the copper converted into oxalate of copper and ammonia (this vol. p. 393 β), and deposited from the solution by electrolysis, the phosphoric acid being estimated in the separated liquid.

3. If the bronze contains *zinc*, this is deposited along with the copper in the process described in 2. The weight of both metals is first determined, and they are then brought into solution as nitrates or sulphates, from which the copper is deposited alone, by electrolysis, and the zinc ascertained by difference.

II. Alloys composed chiefly of Lead and Tin (fine solder, &c.).

First Method.

About 1·5 grams of the powdered alloy is treated with nitric acid as in Vol. I. p. 278, 1 *a*, evaporated almost to dryness, and the hydrated metastannic acid filtered off. The filtrate is then evaporated with the addition of pure dilute sulphuric acid, until the nitric acid is driven off, and the lead determined as sulphate of lead according to Vol. I. p. 244, 3 *a* β. If the alloy also contains other metals, these are found, at all events in part, in the liquid filtered off from the sulphate of lead, so that this should be tested with sulphuretted hydrogen and sulphide of ammonium.

After the hydrated metastannic acid has been converted into stannic oxide and weighed (Vol. I. p. 278, 1), an aliquot part of it is fused with liver of sulphur, or with sulphur and carbonate of soda (Vol. I. p. 475 β), the melt is treated with water, and the undissolved sulphide of lead, after being washed, is dissolved in hot dilute nitric acid, the lead determined in the solution as sulphate, and the filtrate tested for iron, &c.

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* His "Quantitative Analyse auf elektrolytischem Wege," p. 19.

If an insoluble residue is left on heating the lead sulphide with nitric acid, it must be again fused with potassium sulphide, &c., after heating to redness. Another aliquot part of the stannic oxide must be examined for silicic acid by Khittel's method (Vol. I. p. 478). The lead oxide, &c., thus found, together with the silicic acid, must be deducted from the weight of the impure stannic oxide, and in this way the weight of the pure stannic oxide is ascertained.

Second Method.

The finely divided alloy is fused with 3 parts of sulphur and 3 parts of carbonate of soda, or with 4 parts of liver of sulphur, with exclusion of air, and the fused mass heated with water; the sulphide of tin mixed with sulphur is thrown down from the solution by means of dilute sulphuric acid, and after washing is converted into stannic oxide by ignition (Vol. I. p. 279, 280). The residual sulphide of lead left on treating the mass with water is heated with dilute nitric acid, the lead removed from solution by evaporating with sulphuric acid, &c. (Vol. I. p. 244, 3 *a*, *β*), and the filtrate tested for other metals.

Third, Classen's* (*Electrolytical*) *Method.*

The alloy is treated with nitric acid and the process carried out exactly as in the first method; the hydrated metastannic acid containing lead is digested however with strong hydrochloric acid, the greater portion of it evaporated, water added, then an excess of oxalate of ammonia, and the mixture submitted to electrolysis. The tin is obtained on the negative, and the lead with which it was still mixed, at the positive electrode as peroxide. The electrodes are dried at 100°, weighed, and the amount of metal deposited ascertained by the increase in weight.

III. Alloys consisting chiefly of Tin and Antimony (Britannia Metal, Pewter, &c.).

The widely employed tin-antimony alloys contain both metals in varying proportions. In analysing them, attention must be paid to the lead, copper, bismuth, zinc and nickel, which are occasionally intentionally added to the alloy, and, also in very precise examinations, to the small quantities of the other elements, especially arsenic, occurring as impurities in the tin and antimony. One of the following processes may be used in the analysis.

First Method.

The process is carried out exactly as in Vol. I. p. 487 *a*. If the alloy contains other metals besides antimony, tin, and arsenic, they will be partly with the antimoniate of soda, for instance, the oxides of copper, bismuth, iron and nickel, and partly in the alkaline filtrate containing the stannic oxide and arsenic acid, for example, lead and zinc. It will be easily seen, that on further treatment, the copper and bismuth will be obtained as sulphides along with the sulphide of antimony, but the iron and nickel will remain in the liquid filtered off from these sulphides; lead and zinc, however, may be precipitated from the solution still containing a large excess of soda by the cautious addition of sulphide of sodium, before adding the hydrochloric acid and passing in sulphuretted hydrogen.

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* His "Quantitative Analyse auf elektrolytischem Wege," p. 17.

Second Method (by C. Winkler).*

From 1 to 1·5 grams of the finely divided alloy is dissolved in a mixture of 4 parts of hydrochloric acid, 1 part of nitric acid, and 5 parts of water with addition of tartaric acid; it is diluted to 300–400 c.c. (if sufficient tartaric acid is present the liquid does not become turbid) and a solution of chloride of calcium is added, so that there are 8 parts of lime present to 1 part of tin; the solution is neutralised with carbonate of potassa, cyanide of potassium is added, and then more carbonate of potassium, so as to precipitate all the lime. The mixture is now heated to boiling, allowed to subside, decanted through a filter, the precipitate boiled once more with fresh water, allowed to settle, and the supernatant liquid filtered into the first. In this way, the main portion of the antimony is obtained in the filtrate. In order to bring the rest of it completely into solution, the precipitate is dissolved in a little concentrated hydrochloric acid, some tartaric acid is added, the whole neutralised again with carbonate of potassa and thrown down a second time with cyanide of potassium, with the gradual addition of more carbonate of potassa. The mixture is boiled, decanted through the filter, boiled three times with renewed quantities of water, decanting through the filter, and finally bringing the precipitate on to the filter and completing the washing. All the antimony and arsenic are now in the filtrate, and all the tin in the precipitate as hydrated stannic oxide along with a good deal of carbonate of lime; this is dried, heated to a strong red heat in a porcelain crucible along with the filter ash, and transferred to a glass beaker, water being added and then dilute nitric acid; this dissolves the lime whilst the stannic oxide is left behind. The latter is collected on a filter, heated to redness and weighed.

In the filtrate, the antimony is estimated as sulphide. If arsenic is also present, it is best to select Bunsen's method (this vol. pp. 352 and 353) for the separation.

IV. Alloys used for bearings (white bearing-metal).

White metal contains tin as the chief constituent as a rule, but the other components vary considerably. Many "white metals," along with tin, usually contain antimony, others zinc. Copper and lead are mostly present in small amount, occasionally however in very large proportion; many likewise contain mercury, and a few nickel. Other metals which are also met with, such as arsenic and iron, are generally only to be considered as impurities. Phosphorus is only met with when phosphor bronze has been employed in the production of the white metal. From the above, it is evident that a qualitative examination must necessarily precede the quantitative analysis of "white metal."

The following is a convenient way of conducting the quantitative analysis.

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* Zeitschr. f. anal. Chem. 14, 163.

1. From $1\frac{1}{2}$ to 3 grams is treated with nitric acid, as in Vol. I. p. 278, 1, *a*, evaporated almost to dryness on a water bath, and the residue treated with dilute nitric acid. If the precipitate does not subside, a little nitrate of ammonia is added. The impure hydrated metastannic acid is collected, and washed with water to which a little nitrate of ammonia may be advantageously added.

2. The undissolved residue contains the whole of the tin, nearly all the antimony, and, as a rule, small portions of lead, copper, zinc, &c. This is separated from the filter, the latter is saturated with a solution of nitrate of ammonia, dried and incinerated, the ash being added to the precipitate, heated to redness and weighed; it is then fused with carbonate of soda and sulphur (Vol. I. p. 475, β), the mass treated with water, filtered, and the undissolved residue washed, and extracted with hot dilute nitric acid; any residue insoluble in the latter, is again fused with carbonate of soda and sulphur, and the operations mentioned above are repeated.

3. In the nitric solution in 2, the small portions of *lead*, *copper*, *zinc* and *iron* usually contained therein are estimated in the manner described for brass (this vol. p. 413).

4. The solution of sulphur-salts obtained in 2 is acidified with dilute sulphuric acid, allowed to settle, filtered and the precipitate washed; the filtrate is evaporated, and the phosphoric acid resulting from any *phosphorus* originally present therein is estimated by precipitation with molybdenum solution, &c. The amount of *tin* is ascertained by subtracting from the weight of the impure stannic oxide the small quantities of metallic oxides found by 3 and any phosphoric acid obtained in 4. The tin may, moreover, be directly estimated by converting the sulphide of tin into stannic oxide and weighing the latter (Vol. I. p. 279, *c*.).

5. If *antimony* is present, perhaps *arsenic* also, the sulphide of tin obtained in 4, and containing sulphur and sulphide of antimony, possibly also sulphide of arsenic, must be oxidised by fuming nitric acid. After evaporating the excess of the latter, the separation and estimation of the metals is performed as in Vol. I. p. 487, *a*.

6. The nitric acid solution filtered from the hydrated metastannic acid in 1, is evaporated with excess of dilute sulphuric acid in order to separate and estimate the *lead* (Vol. I. p. 465, 2). To the solution separated from the sulphate of lead, about 12 per cent. of hydrochloric acid of sp. gr. 1·1, is added, and sulphuretted hydrogen passed in at a temperature of 70°; the precipitate thus formed is collected, washed, and treated with a solution of sulphide of sodium, or—in presence of mercury—with sulphide of ammonium, filtered, and the filtrate mixed with hydrochloric acid. As the precipitate, which consists mainly of sulphur, may contain the rest of the antimony and arsenic, it is treated with a little brominated hydrochloric acid, filtered, and ammonia added in excess; it is then, after long digestion, acidified with hydrochloric acid, and precipitated by means of sulphuretted hydrogen. The small amount of *sulphide of antimony* obtained in this way is collected in an asbestos filtering-tube, and estimated as in Vol. I. p. 273. If *arsenic* is present, treatment of the moist precipitate with carbonate of ammonia is generally sufficient to separate the two.

7. The insoluble residue in 6, left after the treatment with sulphide of sodium or ammonium, and which, as a rule, still contains some

sulphide of zinc, is dissolved, in order to complete the separation of the metals of the fifth group from zinc, in brominated hydrochloric acid, and digested with excess of ammonia; 12 per cent. of hydrochloric acid of sp. gr. 1·1 is added, the solution precipitated again by sulphuretted hydrogen at 70°, filtered, and the filtrate united with the analogous filtrate from 6; the whole is then concentrated by evaporation, and the *zinc* separated from *iron* (and if need be from *nickel*) by Zimmermann's method (this vol. p. 276).

8. The precipitate thrown down by sulphuretted hydrogen in 7, if it consists entirely of *sulphide of copper*, is converted into cuprous sulphide as in Vol. I. p. 257, *a*, and weighed; if on the other hand it also contains sulphide of mercury, the two are separated as in Vol. I. p. 467 (**149**).

9. The estimation of *mercury* as described in 8, usually yields results which are too low, as a small portion of the mercury may be retained by the precipitate of hydrated metastannic acid and lost in the further treatment of the latter. It is advisable therefore to take a separate portion of the white metal for the estimation of the mercury and to heat it in a current of hydrogen in a boat inserted into a glass tube. The loss in weight of the sample corresponds accurately with the amount of the mercury.

D. Preparations of Tin.

The method of analysing tin preparations follows from that described in § 126. For testing crystallised stannous chloride, and "tin salt," some new methods are here given.

1. To test tin salt for the presence of adulterants (sulphate of zinc, sulphate of magnesia, chloride of sodium, &c.), G. Merz [*] recommends the following process: A weighed quantity, about 2 grams, is covered with five parts by weight of absolute alcohol, and the mixture stirred for five minutes. If the tin salt is free from the usual additions insoluble in alcohol, and has been freshly prepared, a clear solution is obtained, on the contrary if it has absorbed oxygen from the air a fine powdery or flocculent precipitate appears, which however, when slight, dissolves on heating the solution, or, if somewhat larger, on adding a solution of hydrochloric acid gas in alcohol. If the tin salt contains the adulterants frequently added, these remain undissolved as broken crystals, which can be filtered off, washed with alcohol, and weighed.

2. If the amount of stannous chloride in tin salt has to be estimated, the following methods, recommended by Fr. Goppelsröder and W. Trechsel,[†] can be employed instead of those described in Vol. I. p. 280.

a. A weighed quantity of dichromate of potassa is dissolved in a little water in a flask, hydrochloric acid is added to the hot, but not boiling, solution, and then the weighed quantity of tin salt, which should be so calculated as not to reduce the whole of the chromic acid. As soon as this has dissolved, a larger quantity of strong hydrochloric acid is added, the mixture heated, and the evolved chlorine passed into iodide of potassium solution, the liberated iodine being estimated according to Vol. I. p. 292. Its amount corresponds with the dichromate of potassa which has not been reduced by the tin salt, that reduced by the tin salt corresponding with the following equation:

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[*] Pharm. Centralhalle, 17, 105; Zeitschr. f. anal. Chem. 15, 487.

[†] Bull. de la Soc. industr. de Mulhouse, 44, 297; Zeitschr. f. anal. Chem. 16, 364.

$$3SnCl + KO,2CrO_3 + 7HCl = 3SnCl_2 + Cr_2Cl_3 + KCl + 7HO.$$

b. The tin salt is dissolved in cold hydrochloric acid, in a bottle fitted with a ground stopper, adding a known quantity of dichromate of potassa. When the action has ceased, an excess of iodide of potassium solution is added, the mixture allowed to stand for five minutes, and the liberated iodine titrated with hyposulphite of soda. This process is based, therefore, on K. ZULKOWSKY's * method of estimating chromic acid, the absolute trustworthiness of which is still somewhat questionable (*loc. cit.*, p. 76). According to GOPPELSRÖDER and TRECHSEL's researches, one and the same specimen of tin salt yielded perfectly concordant results on repeated analyses being made according to method *b*; the greatest difference being 0·51 per cent. in a content of about 96 per cent. of crystallised stannous chloride.

3. If the total content of tin in tin salt has to be estimated, it is dissolved in hydrochloric acid with the addition of some chlorate of potassa, and the tin, after neutralising the bulk of free acid, is determined by precipitation with nitrate of ammonia (Vol. I. p. 279), or it is dissolved in hydrochloric acid and the tin determined electrolytically (this vol. p. 432).

23. ARSENIC COMPOUNDS.

§ 268.

The estimation of arsenic and its separation from other elements is so fully described in §§ 127, 164 and 165 of the first volume, and the analysis of arsenical ores, alloys, &c., in their respective places in this volume, particularly under pyrites (p. 353), fahlerz (p. 384), the varieties of copper (pp. 401 and 407), the ores of bismuth (p. 419), and of antimony (p. 424), that there is no occasion to revert to the analysis of arsenical compounds in this place. The only object in doing so is to direct attention to a method peculiarly adapted for the determination of small quantities of arsenic in large amounts of ochres and of other pigments which contain very small quantities of arsenical compounds as an impurity; this solves a problem which of late years has frequently presented itself to chemists when they are called on to decide whether a colour may or may not be used for wall paper, &c. To solve this question, it is generally necessary to work with large quantities of the substance, 50 to 100 grams for example, that is quantities to which fusion with carbonates and nitrates of the alkalies, or with liver of sulphur, or treatment with sulphuretted hydrogen in a solution obtained by the use of strong acids, is but little adapted.

The best way is to employ SCHNEIDER† and FYFE's‡ method of distillation, which as is well known has been frequently and carefully investigated by others,§ particularly HAGER's || modification, which

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[*] Zeitschr. f. anal. Chem. 8, 74.

[†] Wiener akadem. Berichte, 6, 409; Poggend. Ann. 85, 433.

[‡] Journ. f. prakt. Chem. 55, 103.

[§] Zeitschr. f. anal. Chem. 14, 250 *et seq.*

[||] HAGER, "Handbuch der pharmac. Praxis," i. 492.

has recently been again recommended by **Emil Fischer**,* and tested by him with reference to the simultaneous presence of antimony and tin. By these modifications it is possible, as is well known, to volatilise the chloride of arsenic and carry it over in the distillate, when it is present as arsenic acid.

The substance (about 100 grams) contained in a long necked round bottomed flask, of about 600 c.c. capacity, is covered with about 100 c.c. of fuming hydrochloric acid of sp. gr. 1·15 and quite free from arsenic. If it should be feared that the decomposition and dissolution of the arsenical compound will not be thoroughly effected in this way a few grams of chlorate of potassa is added. After prolonged action in the cold, 50 c.c. of water is added, and the whole gently warmed for some time, until everything that is soluble has passed into solution. If chlorate of potassa has been employed, a solution of ferrous chloride † perfectly free from arsenic is added until it is in excess, and then another 20 c.c. of the ferrous chloride solution. If hydrochloric acid alone has been used, one addition of 20 c.c. of the ferrous chloride solution is enough.

The mixture is now distilled. As cork connections easily give rise to blackening of the distillate and even caoutchouc stoppers are better avoided, a tubulated retort is employed as the distilling vessel. The neck is directed so as to slope upwards and it is drawn out at the end, and the drawn out part bent obliquely downwards, so that it can be conveniently inserted deep enough into the tube of the condenser. A small flask, into which the lower extremity of the condensing tube is inserted serves as receiver. The contents of the retort are now heated to boiling so that 2 to 3 c.c. pass over per minute, the distillation being continued until only about 30 to 40 c.c. of the liquid remains in the flask. When it has cooled a little, another 100 c.c. hydrochloric acid of sp. gr. 1·1 and free from arsenic is introduced into the retort and the distillation continued as before, the operation being repeated a third time after adding another 100 c.c. of acid, but collecting the distillate which now passes over separately.

The distillates, diluted with water, are separately treated with sulphuretted hydrogen. If the last portion gives no yellow precipitate all the arsenic is contained in the first. If however a precipitate is formed in the last distillate, the distillation must be repeated adding more hydrochloric acid of sp. gr. 1·1 until the final distillate is free from arsenic.

The whole of the sulphide of arsenic is collected on a small filter, washed, digested with a concentrated solution of carbonate of ammonia, filtered, and acidified with hydrochloric acid; sulphuretted hydrogen is passed through it again for a short time, and the sulphide of arsenic thus produced is collected on a small filter, which has been dried at 100° and tared; the precipitate is then washed, dried, and the whole weighed (Vol. I. p. 284).

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* Zeitschr. f. anal. Chem. 21, 266.

† To prepare the solution of ferrous chloride, hydrochloric acid of sp. gr. 1·12 is poured on to very small nails or iron turnings, keeping the latter in excess. As soon as the first violent disengagement of hydrogen is at an end, the mixture is warmed until the evolution of hydrogen almost entirely ceases, and then filtered. After adding 100 c.c. of pure hydrochloric acid of sp. gr. 1·1, to the solution thus obtained it is heated to boiling in a retort fitted with a condenser and receiver, until about 80 c.c. of liquid has passed over. If the distillate, after dilution with water, gives no arsenical reaction when sulphuretted hydrogen is passed into it, it is ready for use, otherwise it must again be heated with fresh quantities of hydrochloric acid until the final distillate is free from arsenic.

If the substance under examination contained any lead, copper, bismuth, cadmium, or mercury, they are wholly left behind in the residue of the distillation; if however antimony or tin is present, small portions of these pass over in the distillate. On this account the latter must be again distilled with the addition of ferrous chloride (a few c.c. up to 30 c.c.); all the arsenic, free from antimony and tin, will be in the distillate, the antimony and tin remaining in the united residues. To attain this object with certainty, it is, according to Fischer, preferable to distil down the first half of the total distillate first obtained, and containing by far the larger portion of the arsenic, by itself with the addition of 3 to 5 c.c. of ferrous chloride until the residue is only 30 c.c., then add the second half, and concentrate to the same volume.

24. Compounds of Phosphorus.

§ 269.

Red (amorphous) Phosphorus.

Red phosphorus, which is manufactured on a large scale, and used in considerable quantities is, as a rule, not absolutely pure. It frequently contains a larger or smaller proportion of ordinary, colourless phosphorus, and as this gradually oxidises on exposure to air varying quantities of phosphoric and phosphorus acids are produced, and on this account the substance has an acid reaction and becomes moist from absorption of water.

For the estimation of these constituents the following process, devised by E. Luck and the author,* is adapted.

1. Estimation of the phosphoric and phosphorus acids contained in amorphous Phosphorus.

About 5 grams of the amorphous phosphorus to be examined is placed evenly in an asbestos filter tube, crushing any lumps there may be, and extracted with water, preferably with the help of the water pump, as long as the washings have an acid reaction. The liquid is then made up to 250 c.c,

1. 100 c.c. of the liquid is evaporated on a water bath with the addition of 5 c.c. of concentrated nitric acid, until the residue is about 1 c.c.; a few drops of red fuming nitric acid is then added, the mixture warmed again for a short time, and the phosphoric acid thrown down in the usual manner by magnesia mixture. (If, in special cases, a turbidity is produced on saturating with ammonia *before* precipitating with magnesia, that is, if the phosphoric acid to be estimated is impure, it is advisable to first precipitate with molybdenum solution, Vol. I. p. 307 β.)

From the weighed pyrophosphate of magnesia, the amount of phosphoric acid originally present, together with that produced by the oxidation of the phosphorus acid, can be reckoned.

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* Zeitschr. f. anal. Chem. 11, 63.

2. A second 100 c.c. of the original washings is placed in a glass beaker, some hydrochloric acid and an excess of mercuric chloride solution added, and the whole gradually heated on a water bath for a considerable time at 60° or thereabouts. Some of the clear liquid is poured off, then a further quantity of the mercuric chloride solution is added, and it is noted whether there is any further precipitation on warming, in which case the complete precipitation must be effected by adding more mercuric chloride to the contents of the beaker.

The precipitate of mercurous chloride is collected on a tared filter paper, dried at 100°, and the amount of phosphorous acid corresponding with the mercurous chloride is calculated according to the equation:

$$3HO,PO_3 + 4HgCl + 2HO = 2Hg_2Cl + 2HCl + 3HO,PO_5.$$

2 equiv. of mercurous chloride = 470·92 corresponding with one equiv. of phosphorous anhydride = 55, or = 82 of hydrated phosphorous acid.

During the precipitation of the mercurous chloride, direct sunlight must be excluded, as otherwise the mercurous salt would become grey from separation of metallic mercury.

By calculating the phosphorous acid to phosphoric acid and deducting this from the total phosphoric acid obtained in 1, the difference gives the phosphoric acid originally existing as such in the phosphorus.

2. Estimation of the total amount of red and colourless Phosphorus.

About 0·5 gram of the phosphorus under examination is freed from phosphoric and phosphorous acids by washing with water in an asbestos filter tube as before, and then placed, together with the asbestos, in a flask, which is connected with a U-tube by means of a glass tube bent twice at right angles, the U-tube containing 5 c.c. of red, fuming nitric acid; and the phosphorus is gradually heated to boiling with nitric acid of sp. gr. 1·2, until it is dissolved. The solution together with the fuming nitric acid from the U-tube are then transferred to an evaporating dish, evaporated, and the viscid residue taken up with water, after it has been again evaporated with some fuming nitric acid. It is then filtered, precipitated with magnesia mixture, and from the phosphoric acid obtained, the total of both the modifications of phosphorus is calculated.

3. Estimation of the red Phosphorus.

About 0·5 gram of the sample is washed thoroughly with water in an asbestos-tube as before until the effluent is no longer acid; the tube is then placed in a second flask, and the water which moistens the phosphorus is removed by washing it first with absolute alcohol and finally with anhydrous ether. The alcoholic and ethereal washings are laid aside, and the phosphorus, which by the preceding operation has become capable of being moistened with carbon bisulphide, is treated with the latter until a few drops evaporated on a watch-glass in the dark, no longer exhibit any luminous appearance. The solution of the colourless phosphorus in carbon bisulphide is collected in a dry flask and laid aside for further use.

A current of dry carbonic acid is passed through the tube containing the washed red phosphorus, first at the ordinary temperature and later at 40° to 50°, and the red phosphorus estimated either by direct weighing, or better, as pyrophosphate of magnesia, after converting it into phosphoric acid by means of nitric acid.

4. Estimation of the ordinary (colourless) Phosphorus.

The carbon bisulphide solution from 3 is introduced into a dry, tubulated retort connected with a condenser, sufficient iodine added to produce a violet tinge, and the mixture distilled almost to dryness on a water bath. The carbon bisulphide which passes over should be tinged with iodine, in order that there may be no doubt that the quantity of iodine added is sufficient. (At least 3 equiv. of iodine must be used for each equiv. of phosphorus.)

The alcoholic ethereal filtrate used for removing water from the phosphorus is added to the residue in the retort, and this is also distilled. The white phosphorus, soluble in carbon bisulphide, will now be found in the residue in the form of tri-iodide of phosphorus, but the small amount of water in the added alcohol-ether solution usually suffices to effect its decomposition into HI and $3HO,PO_3$, or $3HO,PO_5$. Some more water is added, and a portion of the excess of iodine is distilled off along with this, the contents of the retort are transferred to an evaporating dish, some nitric acid added, the whole heated on a water bath until all the iodine is volatilised and the residue is taken up with a little water; the phosphoric acid is then precipitated by molybdenum solution,* estimated as pyrophosphate of magnesia, and from this the amount of the white phosphorus is calculated.

5. Any *foreign admixtures* in the commercial article, such as sand, &c., are best determined by treating the sample with iodine and water in a flask, filtering and weighing the undissolved residues.

When the amounts of both the modifications of phosphorus are known, together with that of the phosphorus and phosphoric acids and the mechanical admixtures, the amount of *water* in the sample can be ascertained by difference.

25. SULPHUR COMPOUNDS.

§ 270.

A. Commercial Sulphur.

Sulphur comes into the wholesale market either as crude sulphur (produced from native sulphur, metallic sulphides, soda waste from the Le Blanc soda process, &c.), or as refined sulphur (roll sulphur, flowers of sulphur). The refined sulphur usually contains only small quantities of impurities, whilst the crude sulphur contains a larger proportion of these. The following method of examination takes cognisance of all the impurities which are usually contained in sulphur.

1. To determine the content of *moisture*, 3 to 5 grams of the coarsely ground sulphur is placed in a weighing glass, dried at 70° (but not longer than necessary) and the loss in weight determined.

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* Commercial iodine frequently contains a little iron, which causes the result to be inaccurate if the phosphoric acid solution is precipitated directly with magnesia mixture.

If the amount of water is to be determined in a larger sample, the tin box described, p. 398 of this vol., and shown in Fig. 120, is employed.

2. For the estimation of *arsenic*, about 10 grams of the sulphur is dissolved in pure potash lye, and chlorine gas prepared from pure materials (free from arsenic) is passed in, until the liquid standing above the precipitated sulphur is clear. Hydrochloric acid is added to the filtrate, and the arsenic (and any antimony present) is estimated by BUNSEN'S method (this vol. p. 352).

If arsenic has been found, it is necessary to examine whether it is present as arsenious acid or as sulphide of arsenic.* For this purpose, a fresh portion of the ground sulphur is treated with dilute hydrochloric acid at a moderate temperature for a long time, filtered and the solution tested to see if it gives sulphide of arsenic when treated with sulphuretted hydrogen. The arsenic obtained in this way is due to arsenious acid present in the sulphur. If the sulphur also contains arsenic as sulphide of arsenic, this can be extracted, by means of aqueous ammonia, from the sulphur that has been treated with dilute hydrochloric acid; it is completely removed, however, only with difficulty. It can be precipitated by acidifying the ammoniacal filtrate, and passing sulphuretted hydrogen through the liquid.

3. For the estimation of any *sulphuric acid* or *chlorine* that may be present, as well as for testing for *sulphurous* and *hyposulphurous acids*, 100 grams of the finely ground sulphur is shaken with 500 c.c. of water, allowed to settle, and filtered.

a. A little nitric acid and nitrate of silver is added to 100 c.c. of the liquid, and any chloride of silver which separates is best converted into metallic silver before weighing (Vol. I. p. 234). If the chloride of silver has a blackish appearance from admixture with sulphide of silver, it is treated with ammonia, filtered, acidified with nitric acid, and the purified chloride of silver converted into metallic silver.

b. 100 c.c. is made just acid with hydrochloric acid, and any sulphuric acid determined by chloride of barium (Vol. I. p. 298).

c. 100 c.c. is tested first as to its reaction; then for the presence of sulphurous or hyposulphurous acid by a few drops of iodide of starch. Subsequently these acids may be quantitatively estimated in another 100 c.c. of the filtrate, by means of a titrated iodine solution (Vol. I. pp. 296 and 297).

4. To determine the *non-volatile substance* (bitumen salts), 10 to 15 grams of the sulphur is carefully heated in a porcelain crucible in a sandbath, until nearly all the sulphur has volatilised (ignition of the sulphur must be avoided). The crucible is then covered with a lid having a hole in it, and pure dry hydrogen gas is passed into the crucible, this being heated until the sulphur has completely volatilised. The residue, consisting of carbon from organic substances and salts, is weighed. It is then carefully heated with free access of air, and weighed again when cold, so as to ascertain the inorganic impurities; and from the difference the amount of the carbon from the organic substances. The inorganic residue can then be further examined if required (for their contents in ferric oxide, lime, magnesia, soda, &c.).

5. One of the following methods can be selected for the estimation of any *selenium* that may be present.

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* See H. HAGER, Pharm. Centralbl. 15, 149; Zeitschr. f. anal. Chem. 13, 346.

a. The very finely powdered sulphur is heated with a large excess of solution of cyanide of potassium for some time, but only so strongly that the sulphur does not cake together, finally boiling and filtering off the undissolved sulphur. The liquid contains sulphocyanate of potassium and, if selenium is present, selenocyanate of potassium. The liquid is supersaturated with hydrochloric acid, so as to throw down the selenium; it must be remembered however that it separates only very slowly from dilute solutions, requiring several days for complete precipitation. The precipitate is collected on a tared filter, dried at a temperature a little below 100°, and weighed (OPPENHEIM,* H. ROSE†).

b. If the condition of the sulphur is such as to give rise to a doubt whether the selenium has been completely dissolved by heating with the cyanide of potassium solution, the sulphur should be fused with eight to ten parts of cyanide of potassium in a long-necked flask, into which hydrogen is passed, proceeding as described in Vol. I. p. 296, *c.*

c. The sulphur mixed with 3 parts of nitrate of potassa and 3 of carbonate of soda is introduced in small quantities at a time into a crucible heated to low redness. The fused mass, which contains all the sulphur as potassium sulphate and all the selenium as selenate, after being heated with water and filtered, is supersaturated with hydrochloric acid, heated with it for a considerable time to convert the selenic acid into selenious acid, and the selenium finally precipitated by sulphurous acid (Vol. I. p. 296).

B. Fuming Sulphuric Acid.

Fuming sulphuric acid, which is now extensively employed in the colour industry and for many other purposes, comes into the market containing a much greater proportion of anhydride than formerly. As the amount of anhydride is variable and is the only constituent paid for, it is frequently subjected to chemical examination; as this presents some difficulties, the following directions will be found useful.

1. If the fuming sulphuric acid, as frequently happens, is either wholly or partially solid, it must first be liquified so as to obtain an average sample. This is best effected by very carefully warming the vessel containing the acid over a sand bath or iron plate (warming in water the author considers to be far more dangerous). During this operation, the stopper should be only loosely fitted in the bottle.

When the acid has become liquid and has been uniformly mixed by careful shaking, about 25 grams of it is transferred in portions, by means of a pipette, into two weighed, light, thin glass weighing bottles with wide necks; these are at once closed by their light hollow stoppers, which should be well ground in, allowed to cool if necessary, and weighed.

One or both of the weighing bottles, according as the examination is to be single or in duplicate, is now placed in a beaker capable of holding a litre, and the glass stopper is taken out and laid in the beaker. Water is now introduced into the beaker by means of a large pipette, but not so much as to render the weighing bottles containing the sulphuric acid unsteady, and cautiously, so that no water reaches the sulphuric acid. The beaker is covered with a close-fitting glass plate, moistened with water on the inside, and left for 24 hours at least, so as to allow time for the acid to absorb water. When this end is attained, more water is put into the beaker and the weighing bottle is overturned so as to bring the acid at once into contact with the whole of the water in the beaker, the latter meanwhile being kept covered.

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* Journ. f. prakt. Chem. 71, 280.

† Poggendorff's Ann. 113, 621; Zeitschr. f. anal. Chem. 1, 76.

There are many divergent opinions as to the best manner of effecting the dissolution in water, and it is often desirable to obtain the solution more quickly than is possible by the above process. In such a case, F. BECKER * recommends weighing the acid in a 10 c.c. platinum crucible with tightly fitting cover, which is plunged (after raising the cover) into a beaker containing 100 c.c. of water, the beaker being immediately covered. Cl. WINKLER † advises weighing products rich in anhydride in stoppered glasses which contain accurately weighed quantities (10 to 15 c.c.) of concentrated sulphuric acid of known acidity, and then allowing the acid to run out into water, or the employment of the tap tube, Fig. 121, which he has designed.‡ The tap should fit perfectly without being greased, and the point be uniformly drawn out. The lower portion is filled $\frac{1}{2}$ or $\frac{2}{3}$ full by means of a suitable suction apparatus, the tap is closed, the tube turned point upwards, the outside wiped clean with paper, and weighed in a horizontal position; the tube is then placed point downwards in water, or—for acids very rich in anhydride—in a layer of coarsely broken crystallised perfectly neutral sulphate of soda, and the contents allowed to run out slowly. Lastly, a drop of water is spirted from above into the tap tube, allowed to remain for a little while, and the tube rinsed out. LUNGE (see last reference) recommends this method of weighing out as the most convenient. In the absence of such a tube, the weighing out may be performed in bulb tubes of about 2 cm. in diameter, terminating at both ends in capillary tubes. From 3 to 5 grams of the acid is sucked up into the bulb tube, which should not be quite half filled, one of the capillary ends, after cleaning, is fused up, the tube weighed in a horizontal position (preferably on a platinum crucible having notches in the edge), and the contents emptied (by breaking off the point) in a manner similar to that described for the tap tube.

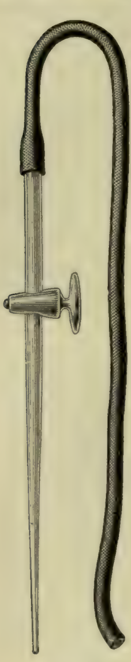

Fig. 121.

Similar glass bulbs are also employed by CLAR and GAIER.§ For weighing off the *anhydride*, they recommend the use of a glass bottle, 58 mm. high and 17 mm. wide, with a high, ground stopper, expanded into a bulb at the top, and having at the point a small opening closed by a glass stopper; the inside of the stopper is filled with slightly moistened glass-wool. The prepared weighed bottle with its contents is placed upside down in a flask of about 2 litres capacity, which contains about 500 c.c. of water at 50° to 60°, and is held aslant. After mixing has been effected through the small opening in the stopper, and after cooling and absorption of the vapour, the solution is made up to 1 litre. If one or other of these methods has been employed, all the sulphuric acid is in solution, and when sulphurous acid is present a portion of this also, the remainder of the sulphurous acid having been volatilised by the heat produced in the liquid. First take the simplest case, that is when sulphurous acid is not present. The diluted acid when quite cold is transferred to a measuring flask, diluted to the mark, mixed, and aliquot parts of the liquid are titrated with the utmost accuracy with normal caustic soda (this vol. p. 194); from the soda used, the corresponding amount of anhydrous sulphuric acid (SO_3) in the whole liquid is calculated, and the value thus obtained is deducted from the fuming acid taken; the difference gives the water of hydration, and from this the amount of monhydrate can be ascertained. By finally deducting the weight of the latter from that of the fuming acid, the amount of sulphuric anhydride existing therein as such is ascertained.

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* Chemikerzeitung, 4, 600; Zeitschr. f. anal. Chem. 20, 302.

† Chem. Industr. 1880, No. 6; Zeitschr. f. anal. Chem. 20, 302.

‡ LUNGE, Taschenbuch für Soda- etc. Fabrikation, Berlin, Jul. Springer, 1883, p. 120.

§ Chem. Industr. 4, 251; Zeitschr. f. anal. Chem. 21, 441.

The influence of the presence of sulphurous acid has now to be considered.

a. If the whole of the sulphurous acid remains in the acid liquid, then the amount of sulphuric anhydride corresponding with the total sulphuric and sulphurous acids is calculated from the amount of caustic soda used. If this is deducted from the fuming acid taken, the number obtained representing water of hydration and therefore also that for monhydrate is too low; consequently the number for the anhydride is too high.

If, on the other hand, we suppose

b. That the sulphurous acid is completely volatilised from the acid solution, then, instead of the amount of water of hydration, the figures will represent this together with the sulphurous acid. The monhydrate is therefore reckoned too high and the anhydride too low.

As in reality, by the methods of estimation given above, part only of the sulphurous acid is volatilised, the rest remaining behind, the result obtained lies between *a* (too high) and *b* (too low) that is, is approximately correct, and, as the estimation of the sulphurous acid is generally considered as too tedious, the analyst is contented as a rule with the results obtained in this way.

If greater accuracy is desired, not only must the acidity of the acid liquid be estimated, but also the amount of sulphurous acid in a separate quantity; this may be accomplished as in Vol. I. p. 296, by iodine solution, or also by means of a solution of permanganate of potassa standardised by iron (WINKLER*). As very dilute liquids have to be employed, it is advisable to deduct from the amount of titrating liquid used, the quantity of iodide of starch or permanganate of potassa required for the coloration of an equal bulk of acidified water.

The calculation is made as follows:

After the acidity of the acid solution and its content of sulphurous acid have been ascertained, the latter is calculated to anhydrous sulphuric acid and the quantity of soda solution corresponding with this is subtracted from the actual amount of the latter used. The sum of the anhydrous sulphuric acid and of the sulphurous acid thus obtained, when subtracted from the weight of fuming sulphuric acid taken, gives the water of hydration contained in it, and from this the monhydrate is known. Lastly, by deducting the latter, together with the sulphurous acid, from the fuming acid taken, the difference gives the content of sulphuric anhydride.

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* Zeitschr. f. anal. Chem. 20, 304.

This method however can only yield accurate results when the dissolution of the fuming acid is so carefully effected, with exclusion of atmospheric air, that the whole of the sulphurous acid in the fuming sulphuric acid actually passes into the acid solution.

26. NITROGEN COMPOUNDS.

§ 271.

A. Nitrose.

The name "nitrose" is applied to the acid which issues from the foot of the Gay-Lussac towers in the manufacture of sulphuric acid. It consists chiefly of a solution in sulphuric acid (of about 76 per cent. monhydrate) of the so-called lead chamber crystals, that is of nitrosulphonic acid or nitrosylsulphuric acid; it may also be regarded, however, as a solution of nitrous acid in sulphuric acid of the above concentration. According to LUNGE * normal nitrose contains no nitric acid. As the amount of nitrous acid varies between 1 per cent. and 2·5 per cent. by weight, and a knowledge of this amount is of importance in working the chambers, nitrose is often the subject of chemical examination.

One of the following methods will serve to estimate the amount of nitrous acid.

1. LUNGE's † modification of the FELDHAUS process (see Vol. I. p. 298).

To carry this out, a solution of permanganate of potassa containing exactly 15·813 grams of the solid salt per litre is required, 1 c.c. of such a solution is capable of yielding 0·004 gram of oxygen and will convert 0·0095 gram of nitrous acid into nitric acid.

To carry out the estimation, 100 c.c. of water is heated to 40°, or at the most 45°, 20 c.c. of the permanganate of potassa solution is added to it, and the nitrose to be tested is then allowed to run in very gradually from a burette furnished with a glass tap, with constant stirring or repeated shaking, until the liquid is just decolorised. As 20 c.c. of the solution of permanganate of potassa correspond with 0·190 gram of nitrous acid, the amount of nitrose required for the decolorisation contains 0·190 gram. For very strong nitrose, 40 c.c. of the permanganate of potassa solution is employed, diluted with 200 c.c. of water.

It is evident that the process can only yield useful results when other substances having a reducing effect on permanganate of potassa (arsenious acid, sulphurous acid) are either absent or present only in traces; also that LUNGE's modification consists in adding the nitrose to the solution of permanganate of potassa until decolorisation takes place, whilst FELDHAUS adds the permanganate of potassa to the very dilute solution of nitrous acid.

2. WALTER CRUM's method, which was further improved by JOHN

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* Berichte der deutsch. chem. Gesellsch. 10, 1078.

† *Ibid.* 10, 1075; LUNGE, "Taschenbuch für die Sodafabrikation," &c., Berlin (of Jul. Springer), 1883, p. 114.

Watts and recommended by Davis, is now very conveniently carried out by using the nitrometer devised by Lunge.*

The process is based on the fact that the acids of nitrogen when dissolved in sulphuric acid are reduced by the action of metallic mercury to nitric oxide, the volume of the latter serving to determine their amount. It follows therefrom, that the amount of nitrous acid can only be correctly ascertained by this method when no other oxygen compound of nitrogen is present, also that when nitrous and nitric acids are simultaneously present the nitrogen of both is obtained as nitric oxide.

Lunge's nitrometer is shown in fig. 122.

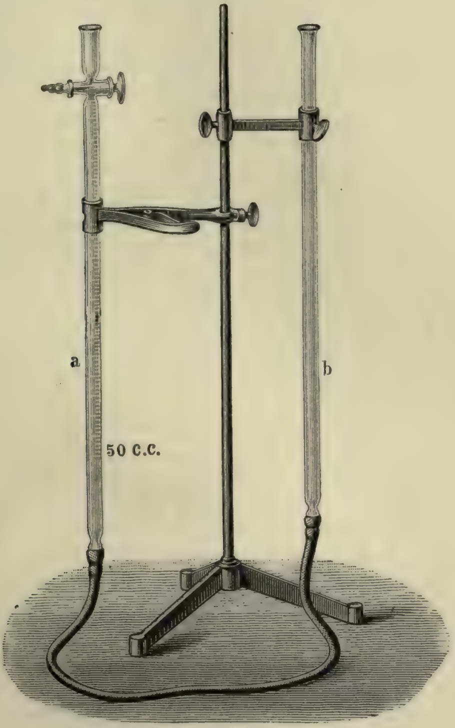

Fig. 122.

The cylindrical measuring tube *a* contains more than 50 c.c. and is graduated in $\frac{1}{10}$ c.c. The plug of the glass tap has two holes bored in it, one straight through, by which communication is established between the funnel of the measuring tube, and a second, bent so as to run parallel with the axis of the plug and allow the contents of the funnel to run out at the side. The tap may also be so turned that the funnel is shut off from both of these holes. To prevent any possibility of the plug falling out, it is secured by fine copper wire to the constriction of the funnel, and is lubricated with a little vaseline in order to make it air tight, taking care however that no vaseline enters the holes in the plug. The tube *b* is a strong glass tube of about the same diameter and capacity as *a*. The two are connected by a strong india-rubber tube. The rest of the arrangement is seen from the figure.

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* See his "Handbuch der Sodaindustrie," vol. i. p. 59, and vol. ii. p. 932; his "Taschenbuch für die Sodafabrikation," &c., p. 116; Ber. deutsch. chem. Gesell. 11, 438; Zeitschr. f. anal. Chem. 19, 207.

In working with the apparatus, the tube *b* is so placed that its lower extremity stands a little higher than the tap in *a*, and mercury is poured in through *b*, the tap being open, until it ascends into the funnel on *a*. The tap is then closed, the mercury in the funnel run off through the side opening in the tap, and *b* is lowered. A measured quantity of nitrose, 2 to 5 c.c. of weak nitrose or only 0·5 c.c. if strong, is now introduced into the funnel by means of a fine pipette and, by carefully opening the tap, it is allowed to run down into *a* without carrying any air along with it, and the funnel is rinsed twice in the same manner, first with 2 to 3 c.c. and the second time with 1 to 2 c.c. of pure concentrated sulphuric acid. It is not advisable to have, altogether, more than 8 to 10 c.c. of acid in the apparatus and it is better to work with less. The amount of nitric oxide produced must in no case exceed 50 c.c. and the vacant space in the tube *a* below the graduation must be large enough to obviate the risk of any of the acid passing into the rubber tubing even if 50 c.c. of nitric oxide should be evolved. In any case, to ensure success, an excess of strong sulphuric acid must be present, and, when the acid which is being analysed is rich in nitrogen acids, a fairly large amount—about 5 c.c.—of concentrated sulphuric acid must be used for rinsing, as otherwise the unavoidable, but usually harmless, separation of mercurous sulphate dirties the measuring tube too much.

The tube *a* is now taken out of the spring clip and shaken thoroughly. The evolution of gas begins at once, and the acid becomes of a violet colour. (In the case of sulphuric acid containing nitric acid, instead of nitrous acid like nitrose, the evolution of gas only begins after shaking a few times.) The evolution of the gas is assisted by inclining the tube several times until it is nearly horizontal and then quickly restoring it to an upright position, so that the mercury falls through the acid; as soon as some gas has collected, the shaking becomes easy. The reaction is complete in one or two minutes (5 minutes are very seldom necessary). When the acid has become clear and has cooled, and the froth has disappeared, which usually does not take long, the tube *b* is raised, the level of the mercury in it adjusted so as to be so much higher than it is in *a* as will correspond with the sulphuric acid (1 mm. height of mercury is equivalent to 7 mm. of sulphuric acid); the volume of the nitric oxide is read off, reduced to 0° and 760 mm. pressure and from this the amount of nitrous acid (or for liquids containing nitric acid, the latter) is calculated by reckoning 1·701 milligrams NO_3 (or 2·417 milligrams NO_5) for each c.c. of nitric oxide at 0° and 760 mm.*

When the reading off is finished, the next thing is to check the accuracy of the compensation of the acid layer by the column of mercury.

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* LUNGE has calculated special tables for the use of the nitrometer, both for reducing gas volume to normal temperature and pressure, as also for calculating the nitric oxide so reduced, into oxygen compounds of nitrogen. See Dingler's Polyt. Journ. 231, 522, and LUNGE's "Handbuch der Sodaindustrie," vol. ii. pp. 922–932.

This is done by opening the tap, when, if the level of the acid rises, the pressure has been too great and a larger volume of nitric oxide should have been read; if on the other hand it falls, the pressure was insufficient and the volume read off too large. If, for example, 15·33 c.c. have been read off, and the acid rises to 15·2 c.c. when the tap is opened, the correct volume is represented by $15·3 + 0·1 = 15·4$. The tube *b* is now lifted so as to drive out first the nitric oxide into the funnel, and then the acid liquid rendered turbid by mercurous sulphate. When the mercury has just entered this, the tap is shut, turning it so as to allow the acid to run off through the hole at the end of the plug into a vessel placed below, the last traces being removed with blotting paper; the tap is then turned so that the funnel communicates neither with the tube *a* nor with the axial opening; and the apparatus is now ready for a fresh analysis. The accuracy of the result is not affected by the acid used containing arsenious acid, organic matter, &c. Should it contain appreciable quantities of sulphurous acid a little powdered permanganate of potassa is added to the acid in the funnel of the nitrometer.

B. Chamber Acid, &c.

Under this section are considered the products containing nitrous acid and nitric acid, arising in the manufacture of sulphuric acid, as is the case for example in chamber acid. Liquids containing peroxide of nitrogen, N_2O_4, can always be considered as if they consisted of 1 equiv. of nitric acid to 1 equiv. of nitrous acid.

The estimation of the acids of nitrogen in sulphuric acid containing both nitrous acid and nitric acid, always necessitates two separate analyses, one for determining the amount of nitrous acid, the other to ascertain the sum of both acids, expressed either as nitrous acid or nitric acid.

1. Estimation of the Nitrous Acid.

The method employed is simply that described in § 271 A. 1. If the acid contains other substances (arsenious acid, sulphurous acid) capable of reducing permanganate of potassa, the estimation is naturally only exact when these are estimated separately and the corresponding correction made. This circumstance has naturally to be considered not only in the estimation of nitrous acid by permanganate of potassa, but also to an equal extent in all the processes for converting nitrous acid into nitric acid (chromic acid method, "chloride of lime" method).*

2. *Estimation of the Nitrous, together with the Nitric Acid.*

This is most easily effected by the method described in § 271, A. 2, using Lunge's nitrometer. It can also be performed in nearly all the ways recommended in § 149, especially § 149 d. α. or β (Vol. I. pp. 392 and 394), or § 149, e. (Vol. I. p. 397). Lunge † makes use of Pelouze's method (§ 149 d. α.), employing ferrous sulphate instead of ferrous chloride, in the following manner.

The iron solution used contains 100 grams of pure ferrous sulphate and 50 grams of pure concentrated sulphuric acid per litre, and for titration a solution containing 15·813 grams of permanganate of potassa per litre is used, the strength being checked as in Vol. I. p. 215 *a.a.* The amount of the permanganate solution requisite to oxidise 25 c.c. of the ferrous sulphate solution is first ascertained. Then 25 c.c. of the latter is put into a flask (fig. 123) furnished with a glass tube and a Bunsen caoutchouc valve.* The solution obtained from the estimation of the nitrous acid in § 271, B. 1. (which now contains all the nitrogen in combination with oxygen in the state of nitric acid), is added together with a further and not too small a quantity of pure sulphuric acid, and then 1 to 2 grams of bicarbonate of soda, so as to drive out the air by the carbonic acid evolved. After quickly inserting the cork fitted with the caoutchouc valve, the liquid is heated to boiling and boiled for some time (often for an hour) until all the nitric oxide is evolved and the liquid has in consequence become quite bright. It is now cooled, diluted and titrated again with the solution of permanganate of potassa. From the difference between the quantity consumed now and on the former occasion, the amount of nitric acid is calculated (1 c.c. of the permanganate of potassa of the above strength corresponding with 0·009 gram of NO_5).

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* See Lunge's "Handbuch der Sodaindustrie," vol. i. pp. 58 and 59.

† "Handbuch der Sodaindustrie" (Brunswick, Fr. Vieweg und Sohn), vol. i. pp. 49–51.

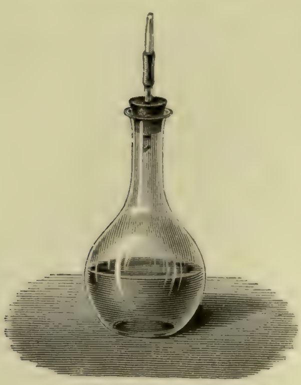
Fig. 123.

As far as the calculation is concerned, the following has to be taken into consideration: If both the acids of nitrogen have been determined as nitric acid, as in LUNGE's modification of PELOUZE's method just described, or by any of the methods in which the nitrogen of the nitrogen acids is converted into ammonia or nitric oxide gas, from which the nitric acid has been calculated, then the amount of nitrous acid found as in 1, is increased in the proportion 38 : 54, that is, it is reckoned into nitric acid; the weight of this is deducted from the total nitric acid found, and the difference gives the amount of nitric acid originally present as such—if however one of the methods based on the oxidation of iron has been employed with a separate sample of the unaltered acid, then the simplest calculation is to consider the oxidation as effected by nitrous acid, that is, 38 parts of nitrous acid are reckoned for each 56 of iron converted from ferrous into ferric chloride, or from ferrous to ferric oxide, deducting from the nitrous acid thus obtained the amount found in 1, and in order to find the content of nitric acid reducing the difference, in the proportion of 114 : 54, that is, in the proportion of 3 equiv. to 1 equiv., as 3 equiv. of nitrous acid give as much oxidising oxygen as 1 equiv. of nitric acid.

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* This can easily be made from a piece of thick caoutchouc tubing closed at the top by a piece of glass rod and having a long slit in the side, which is cut (to a length of 10–15 mm.) by a sharp razor moistened with water, while the tube is bent over the index finger of the left hand. See also KRÖNIG (Zeitschr. f. anal. Chem. 4, 95).

27. CARBON COMPOUNDS.

§ 272.

Under this heading the analysis of graphite, coal and coke is described.

A. Graphite.

Natural graphite, which is used for many purposes, particularly for the production of graphite crucibles and lead pencils, occurs in very different states of purity, and is on that account not infrequently the object of chemical investigation. This alone, however, does not give the value of the different sorts of graphite, as the carbon contained in it is more or less adapted for the manufacture of lead pencils according to its state of division, whilst the differences in degree of combustibility that it exhibits is of importance in the manufacture of crucibles. It is necessary therefore to supplement the chemical analysis by a practical examination based on the uses for which the graphite is intended.

I. Method for complete and accurate analysis.

1. In estimating the degree of *moisture*, a sample is dried at 150°. If the drying is effected in a bulb tube (Vol. I. p. 48) the same portion of substance can also be used for determining the *chemically combined water* (partly present in the alumina); with this object, the contents of the bulb tube are gently ignited in a current of dry air, and the water collected in a chloride of calcium tube (Vol. I. p. 56).

2. The *carbon* in graphite can be most effectively (as the method can be used for *all* kinds of graphite) oxidised by means of chromic acid and sulphuric acid, and the carbonic acid produced collected and weighed in soda-lime tubes. The operation is performed in one of the forms of apparatus described in this vol. pp. 323–327, and by the method given on p. 324, that is, using a sulphuric acid obtained by mixing 2 parts (by weight) of concentrated sulphuric acid with 1 part of water, and an excess of chromic acid, about 5 to 10 grams of chromic acid to 0·25–0·5 gram of graphite.

In many kinds of graphite, the carbon can also be determined by heating it in a current of oxygen, as in an ordinary combustion (this vol. p. 25, *et seq.*). Before however this plan can be adopted with safety, a preliminary examination must be made to see whether it is certain that the carbon of the graphite in question will be completely burned under the conditions obtaining in an ordinary combustion. If the graphite contains carbonates such as, for instance, carbonate of lime, their carbonic acid must be determined and deducted from the total obtained by oxidation with chromic and sulphuric acids or by combustion, before the carbon of the graphite can be estimated from the amount of carbonic acid.

3. The total *mineral constituents* of the graphite can be obtained indirectly by deducting from 100 the carbon, moisture and combined water, expressed per cent. If a direct estimation is required, it is sufficient for many kinds of graphite, to take a small quantity of the finely ground substance (about 0·5 gram, and expose it, with free access of air, in a small platinum crucible, to the long continued strong heat

of a Bunsen or Maste gas burner, see Vol. I. p. 85 (fig. 77). F. Stolba * recommends a platinum crucible with a perforated lid, the round opening in the centre being 5 mm. in diameter. The crucible is placed in an inclined position, and it is covered with the lid so that about a quarter of the opening is left uncovered. The combustion of the carbon is facilitated, if the surface of the graphite is renewed by occasionally turning round the crucible or stirring with a platinum wire. As the operation lasts three to four hours and the weight of the platinum crucible may be affected by such long continued heating, it is necessary to finally re-weigh the crucible. If a muffle is available, the combustion can be carried out in a platinum basin placed in the red hot muffle; this method, which permits of the incineration of large quantities of graphite, is particularly recommended when the ash is to be subjected to further analysis.

If the graphite contains carbonate of lime, the carbonic acid is of course evolved during the heating, and in order to restore it the ash must be repeatedly moistened with a concentrated solution of carbonate of ammonia, dried and gently ignited. A complete agreement between the amount of mineral constituents determined directly and those estimated indirectly, cannot always be expected even after treatment with carbonate of ammonia; for instance when the graphite contains sulphide of iron or hydrated ferrous oxide. Stingl † has directed attention to this circumstance, and quotes examples.

Stolba (see previous reference) did not obtain favourable results on attempting to burn the graphite in a platinum crucible by passing in oxygen, as mineral matters were carried off in the current of gas, and some also fused into globules, which surrounded particles of graphite. As a check, to be certain that the graphite ash contains no carbon, a weighed portion of the finely ground ash may be mixed with pure mercuric oxide, heated to redness in a good draft cupboard and again weighed; ash free from carbon ought not to suffer any loss in weight. The most certain test, however, that the ash is free from carbon, consists in treating a sample of the ash, free from carbonic acid, with chromic and sulphuric acids as in 2, and observing whether carbonic acid is produced or not.

4. To estimate the *individual mineral constituents*, as far as silicic acid, alumina, iron, &c., are concerned, the ash obtained in 3 may be used and treated in the manner prescribed for silicates (Vol. I. p. 348, *b.*), or the graphite may be subjected to a process of disintegration. For this purpose, Wittstein ‡ recommends the following process: About 1 gram of finely powdered graphite is mixed with about 3 grams of carbonate of soda and potassa in a platinum crucible, about 1 gram of potash is placed on the surface of the powder, and the whole heated slowly to redness. The crust formed by fusion must be from time to time broken down with a strong platinum wire. After half an hour's fusion it is allowed to cool, the mass macerated with water, heated to boiling for a quarter of an hour, filtered and washed. The contents of the filter, together with the filter ash, are treated with hydrochloric acid of sp. gr. 1·12, and after digesting for about an hour, water is added, and the residual undissolved carbon is filtered off. The

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* Dingler's polyt. Journ. 198, 213; Zeitschr. f. anal. Chem. 10, 369.

† Ber. deutsch. chem. Gesell. zu Berlin, 6, 391; Zeitschr. f. anal. Chem. 14, 397.

‡ Dingler's polyt. Journ. 216, 45; Zeitschr. f. anal. Chem. 14, 395.

hydrochloric acid solution thus obtained is mixed with the first alkaline solution, hydrochloric acid in excess is added, the whole evaporated to dryness on a water bath, the silicic acid is removed, and the bases in the acid filtrate are estimated (Vol. I. pp. 347 and 348). To be certain that the carbon filtered off contains no more mineral constituents it is burnt; there is no object in weighing this carbon as it represents only a part, about $\frac{4}{5}$ths of the amount originally present.

5. If the graphite contains carbonates, the *carbonic acid* is estimated in a separate somewhat larger sample, according to Vol. I. p. 340.

6. In cases where metallic sulphides (iron or copper pyrites) are present, the *sulphur* is estimated by treating a sample as in this vol. p. 356, 1 or 2. It must not be considered strange if, in employing the first method, the carbon of the graphite remains partly or wholly unoxidised, as many kinds of graphite are not attacked by molten nitrate of potassa (RAMMELSBERG).*

II. Methods for estimating the Carbon alone.

Of the methods proposed for the rapid estimation of carbon in graphite, only that devised by GINTL † will be here described. In this process, a stout tube of highly refractory glass is required, 100 to 120 mm. in length, about 10 mm. wide, and fused together at one end, where it may with advantage be blown out to a moderate sized bulb. From 0·05 to 0·10 gram of the graphite dried at 150° to 180° is placed in this, 1·5 to 3 grams of pure powdered peroxide of lead, previously ignited, is added, the whole weighed and the peroxide of lead carefully mixed with the graphite by a mixing wire; that portion of the tube containing the mixture is now heated, first over a BUNSEN, and finally with a blowpipe lamp until the contents are completely fused and there is no longer any appearance of frothing. According to GINTL, the operation is complete in 10 minutes. The mass is allowed to cool, weighed, and the carbon calculated from the loss in weight—that is the carbonic acid evolved. Of course, the results obtained by this method are only trustworthy if the graphite contains neither combined water capable of being drawn off at 150° to 180°, nor carbonates, and when all the carbon is oxidised by fusion with the peroxide of lead.

GINTL's method is a modification of that of SCHWARZ,‡ in which the lead obtained by fusing the graphite with excess of litharge is weighed (also of BERTHIER's method for estimating the heating value of combustibles applied to graphite). GINTL (*loc. cit.* p. 423) did not obtain satisfactory results by the use of this method.

For the pyrometic estimation of pure graphite, as well as of that containing admixtures of alumina and silicic acid, BISCHOF's § paper on this subject should be consulted.

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* His "Handbuch der Mineralchemie" (2nd edn., W. Engelmann, Leipzig), ii. 2.

† Zeitschr. f. anal. Chem. 7, 425.

‡ Breslauer Gewerbeblatt, 1863, No. 18; Zeitschr. f. anal. Chem. 3, 215.

§ Dingl. polyt. Journ. 204, p. 139.

B. Coal and Coke.

Coal being one of the most important industrial factors, is frequently submitted to chemical analysis, both in its unchanged state and as coke, as it varies greatly in composition, and its value and uses cannot be sufficiently ascertained by external indications. If however such an examination is to have any value, it is above all things necessary to obtain a sample which shall accurately represent the average composition of the coal or coke to be examined. For this purpose, a relatively large amount must be coarsely and uniformly mixed. By breaking up a portion into smaller pieces, samples consisting of lumps about the size of a bean (or for coke, of a hazel nut) can be prepared, and must be stored in stoppered bottles.

1. Estimation of the Water.—When heated at high temperatures, *coal* first yields water and then other liquid constituents; many kinds are also inclined to absorb oxygen at high temperatures. Moreover, as dried coal is also disposed to absorb moisture again from the atmosphere, the exact determination of the amount of water present is not altogether an easy matter. Generally it is considered sufficient to take the loss in weight on drying as representing water, although BRITTON* has directed attention to the circumstance that the results obtained by this method are doubtful, not only for the reasons mentioned above, but because some portion of the water present in coal is firmly combined.

To estimate the amount of water in *coal* by the loss in weight, the tin boxes described in this vol. p. 398, and shown in Fig. 120, are adapted, a few of them being about half filled with the coal broken to the size of a bean. The boxes are then weighed together, and dried at 100° in the water bath described in this vol. p. 398, being weighed from hour to hour until they no longer lose weight.

MUCK † recommends 100° as the most suitable temperature, whilst LUNGE ‡ advises 105°, and HINRICHS § 115°.

To directly estimate the water in coal, a stream of dry air must be passed over the coal heated in a glass tube in an air bath, and then through a weighed chloride of calcium tube, the increase in weight indicating the amount of water given off. Occasionally, a temperature of 100° may be considerably exceeded but it must never go so far as to lead to the evolution of permanently gaseous products of decomposition.

The water in *coke* can be ascertained with certainty from the loss of weight on drying. MUCK (*loc. cit.*) advises drying at a heat which may be as high as 200°, LUNGE (*loc. cit.*) prescribes 110°. Of course, in the case of coke, there is no danger of volatile products of decomposition being formed and passing off with the water during drying.

2. Estimation of the Ash.—The determination of the mineral components of coal and coke is an operation which very often has to be performed. Before describing the best methods, attention should be directed to the circumstance that the yield of ash may vary greatly in

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* Engineering and Mining Journal, 22, No. 7; Zeitschr. f. anal. Chem. 16, 501.

† POST'S "Chem.-Techn. Anal." (Brunswick, Fr. Vieweg & Sohn, 1881), p. 16.

‡ His "Taschenbuch für die Soda-&c. Fabrikation" (Berlin, J. Springer), p. 82.

§ Zeitschr. f. anal. Chem. 8, 133.

one and the same powdered coal, since the mineral constituents present may be left in different states of combination according to the temperature, the duration of the heating, and the admission of air. This is especially the case with coal rich in sulphur, the carbonate of lime being converted into sulphate of lime, and sulphide of iron more or less completely into ferric oxide. According to MUCK,* however, the differences arising from this cause do not exceed 0·1 to 0·2 per cent.

In incinerating, the chief thing is to prevent the coal from caking, as the complete combustion of the carbon is thereby rendered much more difficult. Therefore, when incineration is effected over a gas burner, about 1 to 3 grains of the very finely powdered coal dried at 100° are placed in a covered platinum crucible or covered platinum basin and exposed at first to a gentle heat for a considerable time, whereby not only is decrepitation avoided, which may lead to loss, but also the subsequent caking of the coal. The heating is then continued at low redness with access of air until all the carbon appears to be consumed. In order to shorten this otherwise somewhat tedious operation, LUNGE † advises placing the platinum crucible in the circular opening of an inclined clay tile or asbestos disk, and to heat that part of the crucible which projects below. In this way, the air required for the oxidation does not mix with the gases from the flame, and therefore acts more energetically. A little spirit of wine is now added to the apparently pure ash, and the unconsumed particles of carbon are readily recognised by their colour and buoyancy (MUCK, *loc. cit.* p. 133). After burning off the spirit of wine, the residue is heated to redness again, if necessary, until the object is fully attained, and finally the weight of the platinum vessel is checked.

When a muffle is at hand, several samples can be incinerated at once. They are placed in the cold muffle in flat platinum or porcelain basins, or more conveniently in flat four-cornered platinum trays, then heated slowly, the temperature being gradually raised to redness and maintained there.

Coke requires a much greater heat for the complete combustion of its carbon. On that account it is best to use a muffle in determining the ash constituents; or the object may be obtained by heating the sample in a boat in a current of oxygen.

3. Estimation of Sulphur.—Coal may contain sulphur in three different states of combination—namely, as metallic sulphides, as sulphates, and in the organic matter. The methods for the estimation of sulphur have therefore to be divided into such as give the total amount of sulphur, and those employed for ascertaining the form in which the sulphur is present.

a. Estimation of the total Sulphur.—For this purpose, ESCHKA's method, described in this vol. p. 64, is particularly well adapted. MUCK ‡ advises that the mass, obtained by fusion with magnesia and carbonate of soda, should be treated with hot water, and bromine water added until the liquid remains pale yellow. It is then boiled, decanted through a filter, and washed with hot water; the filtrate is acidified with hydrochloric acid, boiled until the liquid is decolorised, and finally the sulphuric acid (corresponding with the total sulphur in the coal), is precipitated by chloride of barium.

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* Zeitschr. f. anal. Chem. 19, 137.

† His "Taschenbuch für Soda-&c. Fabrikation," p. 83.

‡ POST's "Chem.-Techn. Anal." (Brunswick, Fr. Vieweg & Sohn, 1881), p. 21.

If the reagents employed are not quite free from sulphuric acid, the amount of the impurity must be determined and deducted from the result.

b. Estimation of the Sulphur which is combined with metals and that contained in organic combination.—These portions of the sulphur may either be estimated *indirectly* by deducting the amount found as sulphates in *c.* from the total obtained in *a.*, or *directly* by one of the methods described in this vol. p. 59, 5. According to TSCHIRIKOW* it is advisable, when using SAUER's method, to insert plugs of platinum gauze both in the fore part of the combustion tube, and also behind the platinum boat, especially when estimating the sulphur in coal rich in volatile compounds. Complete combustion is thus ensured, and consequently the passing over of organic products of decomposition into the receiver is prevented.

c. Estimation of the Sulphur present as sulphates (particularly as gypsum).—For this purpose, Crace Calvert's method is used (see this vol. p. 65).

d. Joint estimation of the Sulphur present as sulphides and sulphates.—To effect this and thus obtain also the amount of sulphur present in organic combination by difference, the following method may, according to Th. M. DROWN,† be employed; (the author, however, has no personal knowledge of the method). A saturated solution of bromine in caustic soda of 1·25 sp. gr. is required, and to this so much more caustic soda is added that it no longer gives off free bromine. About 1 gram of the *very finely* ground coal is moistened with about 10 c.c. of this liquid, heated, and then rendered just acid with hydrochloric acid. At intervals of about 10 minutes, two doses of 20 c.c. of the bromine solution are added, the mixture being kept hot, and acidified with hydrochloric acid after each addition. It is now evaporated to dryness, heated at 110° to 115° in order to separate the silica, warmed with hydrochloric acid, filtered, diluted, and the sulphuric acid precipitated by chloride of barium. By this method of treatment, the sulphur in organic combination is not attacked. It should be noted that if the sulphate of baryta is reddish, that is contains iron, it must be purified by fusing with carbonate of soda, according to Vol. I. p. 299.

4. Estimation of Phosphorus.—This is best effected in the ash, a sufficient quantity of coal being incinerated for that purpose; it is then treated for a considerable time with strong hydrochloric acid on the water-bath, finally evaporating to dryness. Hydrochloric acid is added to the residue, then water, the whole warmed, filtered, and evaporated almost to dryness with repeated additions of nitric acid; it is then extracted with water to which nitric acid has been added, precipitated by molybdenum solution, and the phosphoric acid estimated as in § 134, *b.* *β*.

5. Estimation of Nitrogen.—This is effected by any of the methods in this vol. pp. 49–56, using coal dried at 100°.

6. Estimation of Carbon, Oxygen, and Hydrogen.—For this purpose the coal, dried at 100°, may be burnt with chromate of lead

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* Pharm. Zeit. für Russland, 19, 333; Zeitschr. f. anal. Chem. 20, 304.

† Chem. News, 43, 89; Zeitschr. f. anal. Chem. 21, 440.

(this vol. p. 56), or in boats, using a current of oxygen (this vol. p. 25). If the latter method be adopted, a layer of chromate of lead about 10 cm. long, or—according to Muck—of pumice broken to the size of a pea, which has been shaken up with finely powdered chromate of lead, and of course free from water, is placed in the front part of the combustion tube, so that the products of combustion pass first over the glowing granulated oxide of copper and then over the chromate of lead kept at a low red heat. This, as a rule, is sufficient to retain all the sulphurous acid, otherwise, in the case of coals very rich in sulphur, a peroxide of lead tube must also be used (this vol. p. 56).

Before the carbon and hydrogen can be calculated from the carbonic acid and water obtained by the ultimate analysis, it must be ascertained whether the coal or coke contained any carbonates, and also whether any water was present after it had been dried at 100°. In that case the amounts of carbonic acid and water in the sample subjected to combustion (which must be determined in separate portions) must be deducted from those obtained by ultimate analysis.

The oxygen is obtained by difference. As the values for ash, sulphur, nitrogen, hydrogen, and carbon, as well as the possible content of water in the coal dried at 100° influence this, it will be readily understood that the estimation of oxygen by difference cannot be exact. For a *direct* estimation see § 192.

7. Determination of the yield of Coke.—By this is understood the determination of the non-volatile residue produced when the coal is heated in a loosely covered crucible until the evolution of combustible gas ceases. Experience shows that the results obtained by this means may vary appreciably according as to whether a large or small quantity of coal is taken, with the kind of crucible, and also the manner of heating.

Muck,* who has gone thoroughly into this question, gives the following rules which must be followed in order to obtain constant results. A quantity not exceeding 1 gram, and even less with strongly caking coal, is placed in a platinum crucible with a closely fitting lid of large surface, and for very gassy coal over 30 mm. in height. This is placed on a triangle of thin platinum wire, so that the bottom of the crucible is 30 mm. distant from the top of the tube of a Bunsen burner fitted with a chimney, and is heated, using a flame of not less than 18 cm. high, until any flame issuing between the crucible and lid has almost entirely disappeared. By observing these rules, the variations in yield of coke are usually far under 1 per cent. Stronger heating over the blowpipe flame only slightly lowers the production of coke.

To obtain comparative results, the yield of coke must be calculated to coal free from ash. Respecting the influence of the mineral constituents on the production of coke see p. 15 of Muck's work already quoted.

With reference to the method for the gravimetric analysis of gases containing carbonic acid and hydrocarbons, devised by the author, which it was intended to insert in this place (see Vol. I. p. 331), this has been omitted in view of the appearance of Cl. Winkler's admirable

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[*] "Chemische Beiträge zur Kenntniss der Steinkohlen" (Bonn, Max Cohen und Sohn, 1876), p. 14.

treatise on the subject ("Anleitung zur chemischen Untersuchung der Industriegase"), which contains a full description of the methods in question; see the second division of the above-named work, p. 192.

28. HYDROGEN COMPOUNDS.

§ 273.

Peroxide of Hydrogen.

As peroxide of hydrogen of late years has come into use as a bleaching agent and is employed in medicine and surgery, and consequently is manufactured on a large scale, its aqueous solutions, which are put on the market in various degrees of strength, have frequently to be examined chemically. Before describing the methods of estimation, it may be stated that the aqueous solutions of peroxide of hydrogen are not so unstable as was formerly believed, but, if kept from the light, and at a temperature below 30°, lose only a small proportion of their contents.*

Of all the methods for the estimation of peroxide of hydrogen in liquids containing no organic matter, the one resting on the decomposition of the peroxide by means of permanganate of potassa in acid solution, has proved the simplest and most exact. The reaction which occurs, expressed by the equation

$$KO,Mn_2O_7 + 3HO,SO_3 + 5HO_2 = KO,SO_3 + 2MnO,SO_3 + 8HO + 10O,$$

was first observed by **BRODIE** and used by **SCHÖNBEIN** for an approximate, and by **ASCHOFF** for the exact, estimation of peroxide of hydrogen. Among many other chemists, E. **SCHÖNE**† in particular has rendered good service by critically testing this method, as also all others proposed for the estimation of peroxide of hydrogen.

To carry out this method, a solution of permanganate of potassa is employed the strength of which must be proportionate to that of the solution of peroxide of hydrogen. For testing the solutions generally met with in commerce, one containing about 3 grams of permanganate of potassa per litre is suitable. The value of the permanganate solution is ascertained by means of metallic iron (Vol. I. p. 215). In the calculation, it should be noted that 100 c.c. of a permanganate solution capable of converting 0·56 gram of iron from the condition of ferrous oxide to that of ferric oxide, correspond with 0·17 gram of peroxide of hydrogen.

The method of carrying out the operation is very simple. By means of a pipette, a suitable quantity of the peroxide of hydrogen solution (from 2 to 10 c.c.) is put into a beaker containing some 300 c.c. of water strongly acidified with sulphuric acid, and the permanganate solution is run in, stirring meanwhile, until the liquid just retains a permanent reddish tint. Occasionally, according to **SCHÖNE**,‡ especially when the solution of peroxide of hydrogen has been exposed to sunlight, the first portions of the permanganic acid are not imme-

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* See P. **EBELL**'s "Das Wasserstoffhyperoxyd und seine Verwendung in der Technik, Chirurgie und Medecin," paper read before the Hanover district Society of German Engineers, Dec. 9, 1881; Zeitschr. des Vëreins deutsch. Ingenieure, vol. 26.

† Zeitschr. f. anal. Chem. 18, 133.

‡ *Ibid.* 18, 140.

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diately decolorised (the same is also observed in the titration of oxalic acid, Vol. I. p. 217); when once the reaction has begun, however, the fresh quantities of permanganate solution are at once decolorised. BRODIE who first observed this,[*] believed it to be due to the dilution of the solution, but SCHÖNE found that the same thing occurs with relatively strong solutions.

The permanganate of potassa method is suitable for very dilute as well as for concentrated solutions of peroxide of hydrogen, and SCHÖNE obtained good results in the case of solutions containing but a few milligrams per litre (*loc. cit.* p. 142).

Beside this, other methods may be employed, such as bringing the solution of peroxide of hydrogen into contact with iodide of potassium in an acid solution and estimating the liberated iodine with hyposulphite of soda, or it may be decomposed by platinum black, and the evolved oxygen measured (by SCHEIBLER'S apparatus, Vol. I. p. 344), &c., but these methods are neither simpler nor more accurate than titration with permanganate of potassa.

If, however, it is a question of estimating peroxide of hydrogen in liquids containing organic substances, preference must be given to the method of decomposition by platinum black. With regard to this method, it may be remarked that according to EBELL'S experiments (*loc. cit.*), platinum black which has not been ignited decomposes peroxide of hydrogen very quickly, whilst, if ignited, its action, although slower, is equally complete.

If it is required to estimate the peroxide of hydrogen in atmospheric deposits, in which it occurs in exceedingly minute quantities, the above methods are inapplicable. SCHÖNE[†] who has occupied himself with the solution of this problem, makes use of a colorimetric method based upon the separation of iodine from *neutral* iodide of potassium, without addition of ferrous sulphate or any other exciting agent of a similar kind. For details of this method, the reader is referred to the original treatise.

SUPPLEMENT TO SECTION II.

I. ESTIMATION OF GRAPE SUGAR (DEXTROSE) FRUIT SUGAR (LEVULOSE), INVERT SUGAR, MALTOSE, MILK SUGAR, CANE SUGAR (SACCHAROSE), STARCH, AND DEXTRIN.

The estimation of these compounds is often called for in the analysis of agricultural and technical products and pharmaceutical preparations; it is also of importance in the examination of diabetic urine. Some of the best methods for the purpose are therefore given in this supplement.

Setting aside the purely physical processes, which are based either upon the specific gravity of the saccharine solutions,[‡] or upon their behaviour towards polarized light,* the following methods serve for the estimation of the different kinds of sugar.

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[*] Poggend. Annal. 120, 318.

[†] Berichte der deutsch. chem. Gesellsch. 7, 1693; Zeitschr. f. anal. Chem. 14, 90 and 91, and above all 18, 154.

[‡] The BALLING or BALLING-BRIX tables are most frequently used for estimating the amount of cane sugar from the sp. gr. of the solution. These are to be found in many works, such as for example in the "Handwörterbuch der reinen und angewandten Chemie," by LIEBIG, POGGENDORFF and WÖHLER (Brunswick, Fr.

A. Methods based upon the reduction of cupric oxide to cuprous oxide.
B. Methods based upon the reduction of mercury compounds.
C. Methods based upon the decomposition of sugar by alcoholic fermentation.

These methods are described in the following sections.

A. Methods based upon the Reduction of Cupric Oxide to Cuprous Oxide.

§ 274.

I. GENERAL PRINCIPLES.

The fact that a solution of sulphate of copper mixed with tartrate of potassa or of soda, and hydrate of potassa or soda (and which if mixed in the proper proportions remains unaltered when boiled) is decomposed by grape sugar at the boiling temperature, with separation of cuprous oxide, was first made use of by BARRESWIL † for the estimation of sugar; subsequently the method was thoroughly investigated, particularly by FEHLING ‡ who greatly improved on BARRESWIL's prescription for the preparation of the alkaline solution,§ and established

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Vieweg und Sohn, 1859), vol. vii. p. 4; OTTO's "Lehrbuch der rationellen Praxis der landwirthschaftlichen Gewerbe," 5th edition, 1860–1862, vol. i. p. 233; STAMMER's, "Lehrbuch der Zuckerfabrikation," 1874, p. 38; "MUSPRATT's Chemie," 3 edn. by KERL and STOHMANN (Brunswick, Schwetschke und Sohn, 1874), vol. i. p. 194, and vol. vii. p. 694; BOLLEY's "Handbuch der techn. chem. Untersuchungen," 4th edn., by E. KOPP (Leipzig, Felix, 1874), p. 679; FRÜHLING and SCHULZ, "Anleitung zur Untersuchung der für in Zuckerindustrie in Betracht kommenden Rohmaterialien, &c." (Brunswick, Fr. Vieweg und Sohn, 1876), p. 16; POST's Chem. techn. Analyse (same publisher, 1881), p. 694. The BALLING-BRIX tables although compiled for cane sugar only, are frequently used for grape sugar as the difference in density of equal percentages of cane sugar and grape sugar in solution is but slight; see GRAHAM, HOFMANN and REDWOOD, "Jahresber. der Chemie," 1852, p. 803; POHL, "Ber. der Wien Akad." 1854, vol. 11, p. 664; HOPPE-SEYLER, Zeitschr. f. anal. Chem. 14, 305. A comparative table, by which the difference of densities can be seen, is to be found in BOLLEY's Handbuch (see above), p. 681. A special table for estimating grape sugar from the sp. gr. of its aqueous solutions was prepared by SALOMON (Ber. deutsch. chem. Gesell. 14, 2711), and a corresponding one for invert sugar by CHANCEL [Lippmann, "Die Zuckerarten," &c. (Brunswick, Fr. Vieweg und Sohn, 1882) p. 73].

* The estimation of sugar by the polariscope is dealt with in the works just mentioned, the most complete description, however, being LANDOLT's "Das optische Drehungsvermögen organischer Substanzen," &c. (Brunswick, Fr. Vieweg und Sohn, 1879).

† Arch. d'anatomie, 1846, p. 50; Journ. de Pharm, 6, 361; BERZELIUS' Jahresber. 25, 556.

‡ Annal. d. Chem. u. Pharm. 72, 106, and 106, 75.

§ The original FEHLING prescription for the preparation of the copper solution is as follows: Dissolve 40 grams of pure crystallised sulphate of copper, free from adhering moisture, in about 160 c.c. of water; further, dissolve in another vessel 160 grams of neutral tartrate of potassa in a little water, add 600 to 700 grams of pure caustic soda solution of sp. gr. 1·12, pour the first solution gradually into the second, and dilute the clear dark-blue liquid to exactly 1154·4 c.c. at 15°. Calculated to 1000 c.c. and hydrate of soda this gives, if, moreover instead of the former the rule, confirmed afterwards by Neubauer * and others, that 1 equiv. of grape sugar ($C_{12}H_{12}O_{12}$) = 180, reduces 10 equiv. of oxide of copper = 397. This important method has in course of time been subjected to considerable investigation and modification. Latterly Soxhlet,† in particular, has occupied himself with a most thorough examination of the method, and important work on the subject has also been done by Gratama,‡ Ulbricht,§ Märcker, Behrend and Morgen,‖ Rodewald and Tollens,¶ Allihn,** Degener,†† Meissl ‡‡ and others. As the fruit of these investigations, the laws laid down by Soxhlet are here given.

1. The assumption that 1 equiv. of grape sugar (180) reduces 10 equiv. of oxide of copper and that therefore 10 c.c. of Fehling's solution corresponds with 0·050 gram of grape sugar free from water is only correct—or, more exactly, nearly correct—for the degree of dilution prescribed by Fehling (10 c.c. of copper solution + 40 c.c. of water), when a 0·5 to 1 per cent. sugar solution is employed. Soxhlet found, by using a 1 per cent. sugar solution, that the proportion is 1 equiv. = 10·11 equiv. instead of 1 to 10. Hence 10 c.c. of the Fehling solution, under these conditions, correspond with only 0·0495 gram of grape sugar and not with 0·05 gram.

2. If the degree of concentration is altered, the reducing effect of the solution is changed; thus by the use of undiluted Fehling's solution and a 1 per cent. solution of grape sugar Soxhlet found that the proportions were 1 equiv. = 10·52 equiv.

3. The amount of copper solution on which the sugar solution acts influences the reducing effect of the latter. If therefore the sugar solution is run into the boiling copper solution, the first portions, coming in contact with a larger excess of copper, are reduced more than the succeeding portions. The reducing action therefore is not a constant one under these circumstances, but gradually diminishes.

4. Grape sugar, fruit sugar, invert sugar, and maltose, have not an identical, but different reducing effects. Thus by employing the proportions given in 1, that is a Fehling's solution diluted with four measures of water, and a 1 per cent. sugar solution:

10 c.c.	of Fehling's solution	correspond	with	0·0495	gram of	grape sugar ($C_{12}H_{12}O_{12}$).
10	,,	,,	,,	0·0515	,,	invert sugar ($C_{12}H_{12}O_{12}$).
10	,,	,,	,,	0·0740	,,	maltose ($C_{12}H_{11}O_{11}$).

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equivalent reckoned for sulphate of copper (namely 124·75), we take the one now accepted (124·0), 34,639 grams of sulphate of copper, 138·6 grams of tartrate of potassa, and 54·58–63·67 of caustic soda.

* Archiv der Pharm. [ii.] 72, 278.

† Chem. Centralbl. [iii.] 9, 218 and 236; Journ. f. prakt. Chem. ii. 21, 227; Zeitschr. f. anal. Chem. 18, 348 and 20, 425.

‡ *Ibid.* 17, 155.

§ Chem. Centralbl. [iii.] 9, 392; Landwirthschaftl. Versuchsstat, 27, 81.

‖ *Ibid.* 9, 584.

¶ Zeitschr. f. anal. Chem. 18, 605.

** Neue. Zeitschr. f. Rübenzuckerindustrie, 3, 230, and Zeitschr. des Vereins f. Rübenzuckerindustrie 19, 865; Zeitschr. f. anal. Chem. 20, 434, and 22, 448.

†† Zeitschr. des Vereins f. Rübenzuckerindustrie. 18, 349; Zeitschr. f. anal. Chem. 22, 444.

‡‡ *Ibid.* 1879, 1034.

That the reducing effect of milk sugar differed considerably from that of grape sugar was already known, but opinions differed as to the variation. Soxhlet found that 10 c.c. of Fehling's solution corresponded with 0·0676 gram of milk sugar dried at 100° ($C_{12}H_{12}O_{12}$), and further that with milk sugar the dilution of the copper and sugar solutions produced no effect on the result, or only an inappreciable one.

5. By allowing 1 per cent. solutions of the different sugars to act on undiluted Fehling's solution, Soxhlet obtained the following reducing effects:

50 c.c. of Fehling's solution = 0·2375 gram of grape sugar ($C_{12}H_{12}O_{12}$).
,, ,, ,, = 0·2470 ,, invert sugar ($C_{12}H_{12}O_{12}$).
,, ,, ,, = 0·2572 ,, levulose ($C_{12}H_{12}O_{12}$).
,, ,, ,, = 0·3890 ,, maltose ($C_{12}H_{11}O_{11}$).
,, ,, ,, = 0·3380 ,, cryst. milk sugar ($C_{12}H_{12}O_{12}$).

6. The rapidity of the effect of the different sugars on Fehling's solution at the boiling temperature varies, for instance:

Grape sugar required boiling for . .	2	minutes
Invert sugar ,, ,, . .	2	,,
Levulose ,, ,, . .	2	,,
Maltose ,, ,, .	3 to 4	,,
Milk sugar ,, ,, .	6 to 7	,,

Bearing these newly ascertained facts in mind, Soxhlet so modified the volumetric analysis of the sugars by Fehling's method that the results, as far as exactness is concerned, leave nothing to be desired, whilst Märcker in conjunction with Behrend and Morgen showed, Soxhlet recognised, and Allihn, as well as Meissl, more completely demonstrated, that by gravimetric analysis exact results may also be obtained.

II. Methods for the Estimation of Sugar.

The following will be described:

1. Fehling's volumetric method for the estimation of grape sugar, in its original or only slightly modified form, as this is still suited to the approximate estimation of the grape sugar in must, diabetic urine, &c.

2. Soxhlet's modification of Fehling's method, for the more precise volumetric determination of different sugars.

3. Gravimetric methods for the estimation of sugar.

1. Fehling's Method.

As the stability of the copper solution originally employed by Fehling, the preparation of which is described in the note to p. 460 leaves much to be desired, it can be replaced by two solutions: (*a*) an aqueous solution of sulphate of copper containing 34·639 grams of pure crystallised sulphate of copper per litre, and (*b*) a solution prepared by dissolving 173 grams of crystallised tartrate of soda and potassa in water in a litre flask, adding 572 grams of soda solution of sp. gr. 1·12 (containing 60 grams of caustic soda) and filling up to the mark, or, what is preferable, in the case of *b*, as this solution also cannot long be kept unaltered, by dissolving 43·3 grams of tartrate of soda and potassa in water in a 250 c.c. flask adding 143 c.c. soda solution of 1·12 sp. gr. or 15 grams of caustic soda, and making up to 250 c.c.

It will be seen that similar proportions of mixture and dilution are obtained in either case; I. by diluting 10 c.c. of the original FEHLING'S solution (see footnote p. 460) with 40 c.c. of water, or II. by adding to 10 c.c. of the aforesaid alkaline solution of tartrate of soda and potassa, *b*, 10 c.c. of the pure aqueous sulphate of copper solution, *a*, and diluting with 30 c.c. of water.

Either of the two liquids therefore corresponds, under the given conditions (see § 274, I. 1), almost exactly with 0·05 gram of grape sugar.

The sugar solution to be tested is now diluted so as to contain between 0·5 and 1 per cent. of sugar, which can generally be done with the aid of the specific gravity determination. In order to give the necessary indications in this respect for ordinary cases, the following extract from SALOMON'S Table is given:

Grams of anhydrous grape sugar in 100 *c.c. of an aqueous solution at* 17·5°.

Grams grape sugar.	Sp. gr.	Grams grape sugar.	Sp. gr.	Grams grape sugar.	Sp. gr.
1	1·00375	10	1·0381	19	1·0725
2	1·0075	11	1·0420	20	1·0762
3	1·0115	12	1·0457	21	1·0800
4	1·0153	13	1·0495	22	1·0838
5	1·0192	14	1·0533	23	1·0876
6	1·0230	15	1·0571	24	1·0910
7	1·0267	16	1·0610	25	1·0946
8	1·0305	17	1·0649	26	1·0985
9	1·0342	18	1·0687		

A quantity of the above-mentioned dilute copper solution, I. or II. corresponding with 0·05 gram of grape sugar, is heated in a small flask to gentle ebullition, and from a burette, divided into $\frac{1}{10}$ c.c., the sugar solution is run in slowly in small portions at a time. After the addition of the first few drops, the liquid shows a greenish-brown tint, owing to the suboxide and hydrated suboxide suspended in the blue solution; in proportion as more of the sugar solution is added, the precipitate becomes more copious, acquires a redder tint, and subsides more quickly. When the precipitate appears deep red, the lamp is removed, the precipitate allowed to subside a little, and the flask placed on white paper, or held up between the eye and a window so that the liquid may be seen by transmitted light; in this way, the slightest bluish-green tint can be easily detected. To make quite sure, however, a small portion of the clear supernatant liquid is poured into a test-tube, a drop of the sugar solution added, and the whole heated; if the least trace of copper salt remains undecomposed, a yellowish-red precipitate will form, appearing at first like a cloud in the liquid. If this occurs, the contents of the test-tube are poured back again into the flask, and more of the solution of sugar added until the reaction is complete. In the amount of sugar solution used, there is 0·050 gram of grape sugar.

When the operation is completed, the liquid is tested to ascertain whether the exact point of complete reduction has been attained, that is, whether the solution contains either copper, sugar, or a brown product of the decomposition of the latter. For this purpose a portion of the liquid is filtered off while still quite hot. If the exact point has been attained, the filtrate must be colourless, or only slightly yellowish, without the least brownish tinge. The liquid must remain unchanged when heated either with a drop of the copper solution or with a little of the grape sugar solution, or on adding sulphuretted hydrogen to the solution acidified with hydrochloric acid, or ferrocyanide of potassium to the solution acidified with acetic acid. If any excess of either copper oxide or sugar is found, the experiment must be repeated. As a rule, the first experiment gives only an approximate result. In the second experiment, it is best to add very nearly the whole of the required quantity of sugar to the cold copper solution, then heat the mixture, boil for two minutes, and proceed cautiously, adding two drops at a time until the operation is complete.

The results are constant and fairly satisfactory. If the sugar solution is of the requisite strength, 5 to 10 c.c. of it will have to be used in each determination. Care must be taken that the solution of sulphate of copper always remains strongly alkaline; should the sugar solution be acid, it must be rendered feebly alkaline before diluting to the volume determined on.

If this method is employed for diabetic urine, it must be recollected that on boiling urine with soda lye, ammonia is produced which will retain cuprous oxide in solution. As such a solution turns blue by the action of the air, this must be as far as possible avoided, and the hot liquid must only be allowed to stand, for the determination of its colour, so long as is unavoidably necessary to be able to see through the liquid free from cuprous oxide. For the same reason it is unadvisable to filter the liquid when estimating the sugar in urine, neither is there any object in testing the filtrate with sulphuretted hydrogen or ferrocyanide of potassa, as copper (as suboxide dissolved in ammonia) may be, and often is, present in it even when all the peroxide of copper has been reduced by sugar.

2. SOXHLET'S modification of FEHLING'S Method.

a. 34·639 grams of sulphate of copper* is dissolved in water and made up to 500 c.c.

b. 173 grams of crystallised tartrate of soda and potassa, dissolved in 400 c.c. of water, is mixed with 100 c.c. of soda solution, containing 500 grams of hydrate of soda per litre. Naturally, if such a soda solution is not ready to hand, it can be easily prepared by dissolving 173 grams of tartrate of soda and potassa in 400 c.c. in a 500 c.c. measuring flask, adding 50 grams of hydrate of soda, filling up to the mark when quite cold, and mixing.†

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* SOXHLET advises that the commercial chemically pure sulphate of copper should be recrystallised by stirring the hot saturated and filtered solution as it cools and the fine crystalline powder, after being dried by pressing between filter paper, should be spread out on a thin layer in a dry place and left for 24 hours, by which time it will contain the correct amount of water.

† SOXHLET prepares the alkaline solution of tartrate of soda and potassa fresh every day, and says "the use of Rochelle salt solution which has been kept for

c. 25 c.c. of the sulphate of copper solution *a* and 25 c.c. of the alkaline solution of Rochelle salt *b* is placed in a deep porcelain basin,* heated to boiling, and the sugar solution added a little at a time until the liquid, after sufficient boiling, the duration of which must be varied with the kind of sugar (§ 274, I. 6), no longer appears blue. From this preliminary test, the approximate amount of the sugar corresponding with 50 c.c. of the FEHLING's solution is calculated as set forth in § 274, I. 5, and the solution is diluted so as to contain 1 per cent. of sugar, or, more accurately speaking, about 1 per cent.

d. A fresh mixture of 25 c.c. of the copper solution *a* with 25 c.c. of the alkaline solution of Rochelle salt *b* is now heated without diluting it with water, along with a quantity of the approximately 1 per cent. sugar solution, corresponding with the preliminary test (that is about 23 c.c. of grape sugar, 24 c.c. of invert sugar, 25 c.c. of levulose, 38 c.c. of maltose, or 33 c.c. of milk sugar solution) so long as is necessary for the particular kind of sugar operated on (§ 274, I. 6), and the whole is then poured through a relatively large folded filter. If the filtrate is green or appreciably greenish, further testing for copper is naturally unnecessary, but should it on the other hand be yellow then some copper may still remain in solution. To ascertain this, it is acidified with acetic acid as soon as about one-third of the liquid has passed through, and ferrocyanide of potassium is added. A deep red coloration indicates large quantities of copper, whilst a pale rose tint shows that traces only are present; if there is no change of colour, all the copper is precipitated. If there is any copper in the solution, a fresh test is made in precisely the same manner as before only with a larger amount of sugar solution, which is regulated according to the intensity of the copper reaction observed. On the other hand, if no copper is found, a fresh experiment is made taking 1 c.c. less sugar solution.

These trials are repeated until two, in which the difference of the amount of sugar employed is only 0·1 c.c., yield filtrates the one containing copper and the other not. The mean between the two is to be regarded as the exact quantity of the sugar solution necessary to decompose 50 c.c. of the FEHLING's solution. Generally the object will be accomplished in five or six attempts. The calculation is made on the basis of the comparative figures set out in § 274, I. 5. If for example 24 c.c. of grape sugar solution are required, they contain 0·2375 gram of grape sugar, or in the case of maltose solution 40 c.c. will contain 0·389 gram of maltose.

In coloured liquids, it is more difficult to detect the presence of copper in the filtrate by means of ferrocyanide of potassium, and the results are even less certain with the sulphuretted hydrogen test. For such cases, SOXHLET advises boiling the filtrate for about a minute with a few drops of the sugar solution and leaving it to stand quietly for 3 to 4 minutes. If the liquid be now poured out from the beaker and

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some time is to be avoided just as much as with the employment of ready-made FEHLING's solution that has been laid aside for some time, however well the vessel containing it may have been closed." According to the author's experience, it is unnecessary to prepare fresh alkaline Rochelle salt solution daily.

* It will be understood that the 50 c.c. in the basin contains exactly the same amount of sulphate of copper and Rochelle salt in solution as 50 c.c. of the solution prepared according to FEHLING's original formula.

the bottom of the latter wiped out with a piece of white filter paper wrapped round a glass rod, the paper will be coloured red by adherent cuprous oxide should there be any copper in the filtrate. Larger quantities of copper in the filtrate will already have been detected by a red deposit on the sides and bottom of the glass.

e. SOXHLET's modification of FEHLING's method is also generally applicable to diabetic urine, but the experimenter must be content, after boiling for two minutes and allowing the liquid to stand for a short time, to determine whether the supernatant liquid is green or not, as the testing for copper in the filtrate is not practicable (see above, FEHLING's Method).

f. As, in SOXHLET's modification, the time of boiling is definitely fixed and is not extended beyond what is just necessary, good results can also be obtained when the reducing sugars are in solution along with substances which reduce FEHLING's solution only after long-continued action. For example grape- or invert-sugar may be estimated by this method in liquids in which cane sugar is also present (see § 277, I.).

3. Gravimetric Methods of Sugar estimation.

a. Determination of Grape Sugar.

This rests on the fact ascertained by MÄRCKER that when grape sugar solution acts on FEHLING's solution at the boiling temperature, there is no proportional relation between the amount of grape sugar and that of the precipitated cuprous oxide, but that a definite relation exists if equal quantities of copper solution are allowed to act under like conditions in all cases. The method therefore rests on a purely empirical basis. MÄRCKER based the formula for the calculation on three estimations only, performed with different quantities of sugar. ALLIHN established a more secure foundation, by making 11 determinations; he also greatly facilitated the performance of the operation by calculating from his results a table from which the relation between the copper thrown down as cuprous oxide and the grape sugar can be found without further trouble. In order that the table may apply, the details of ALLIHN's method must in no way be departed from, as it rests on a purely empirical basis. The reagents required are: *a.* a copper solution prepared by dissolving 34·6 grams of crystallised sulphate of copper in water to 500 c.c.; *b.* a solution of Rochelle salt obtained by dissolving 173 grams of Rochelle salt and 125 grams of caustic potash and making up to 500 c.c. The solutions are kept separate.

Thirty c.c. of the alkaline Rochelle salt solution, *b*, and 30 c.c. of the copper solution, *a*, are put into a beaker holding about 300 c.c. and heated to boiling over a naked flame or sandbath. For each trial, 25 c.c. of the sugar solution (which must not contain more than 1 per cent. of sugar) is run into the boiling liquid from a pipette, the mixture boiled up once more, and the precipitated cuprous oxide filtered off at once. For filtering, an asbestos tube is used, following SOXHLET's directions. ALLIHN recommends preparing it from a piece of combustion tube 10 cm. long, drawn out to about half the width at one end, about one-fourth of the wider part being packed with freshly-ignited, long-fibred, soft asbestos. Under the asbestos in the conical part of the filter tube (*a.* in Fig. 124), a small wad of glass wool is placed to prevent the asbestos fibres being carried through during filtration. The asbestos must be packed neither too loosely nor too tightly, as in the first case some of the cuprous oxide might easily run through, and, in the second, filtration would be too slow. It is well to place a loose asbestos wad on the top of the tolerably tightly packed mass; the cuprous oxide then distributes itself in the former instead of forming a close adherent layer hindering the filtration, as it would otherwise do.

The prepared filter-tube is now carefully heated over a lamp, a stream of dry air being drawn through it meanwhile so as to remove all moisture; after cooling in a desiccator it is weighed. When in use, the filter-tube, as shown in the figure, is provided with a small funnel, fitting into a bored cork, and, in order to promote rapid filtering, the flask receiving the filtrate is connected with the pump. After repeated decantation, the cuprous oxide is brought on to the filter, washed with cold water, and finally rinsed with alcohol and ether to facilitate drying. The traces of suboxide adhering to the beaker are removed by a glass rod covered at the end with a piece of caoutchouc tubing. It is best dried in a heated air-bath, this taking barely a quarter of an hour.

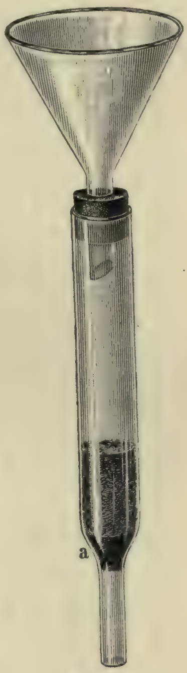

Fig. 124.

The reduction of the cuprous oxide is now proceeded with, as the metallic copper obtained from it has to be weighed. For this purpose, the filter-tube is fixed in an inclined position and moderately heated while a current of pure, dry hydrogen gas is passed through it. As the reduction takes place even at a moderate heat (according to Soxhlet's experiments, already at 130° to 135°), it is unnecessary for the flame to come in contact with the tube, and care must be taken to avoid heating that portion of the tube containing the glass wool, or the lead oxide it contains may be reduced. As soon as the precipitate has assumed the characteristic colour of copper, and drops of water cease to form on the cold end of the tube, which generally occurs after a few minutes, the object is attained. It is now allowed to cool in the current of hydrogen, dry air is then passed through for a short time and the whole weighed. The amount of copper obtained (in milligrams) is looked up in the accompanying table (pp. 468, 469) and the corresponding amount of grape sugar read off in the adjacent column.

b. Estimation of Invert Sugar.

Invert sugar, although otherwise behaving towards an alkaline copper solution, mixed with an alkaline tartrate, almost exactly in the same way as grape sugar, has a different reducing effect from the latter, as Soxhlet has shown; Allihn's Tables for grape sugar, therefore, cannot be used for invert sugar, and the construction of a new set of tables in an empirical manner becomes necessary. For such a one we are indebted to Meissl.*

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* Zeitschrift des Vereins für Rübenzucker-Industrie, 1879, 1034.

Table for calculating Grape Sugar from the amount of Copper found by Gravimetric Analysis.

Copper.	Grape sugar.	Copper.	Grape sugar.	Copper.	Grape sugar.	Copper.	Grape sugar.	Copper.	Grape sugar.	Copper.	Grape sugar.	Copper.	Grape sugar.	Copper.	Grape sugar.
Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
10	6·1	39	20·4	68	34·8	97	49·4	126	64·2	155	79·1	184	94·2	213	109·5
11	6·6	40	20·9	69	35·3	98	49·9	127	64·7	156	79·6	185	94·7	214	110·0
12	7·1	41	21·4	70	35·8	99	50·4	128	65·2	157	80·1	186	95·2	215	110·6
13	7·6	42	21·9	71	36·3	100	50·9	129	65·7	158	80·7	187	95·7	216	111·1
14	8·1	43	22·4	72	36·8	101	51·4	130	66·2	159	81·2	188	96·3	217	111·6
15	8·6	44	22·9	73	37·3	102	51·9	131	66·7	160	81·7	189	96·8	218	112·1
16	9·0	45	23·4	74	37·8	103	52·4	132	67·2	161	82·2	190	97·3	219	112·7
17	9·5	46	23·9	75	38·3	104	52·9	133	67·7	162	82·7	191	97·8	220	113·2
18	10·0	47	24·4	76	38·8	105	53·5	134	68·2	163	83·3	192	98·4	221	113·7
19	10·5	48	24·9	77	39·3	106	54·0	135	68·8	164	83·8	193	98·9	222	114·3
20	11·0	49	25·4	78	39·8	107	54·5	136	69·3	165	84·3	194	99·4	223	114·8
21	11·5	50	25·9	79	40·3	108	55·0	137	69·8	166	84·8	195	100·0	224	115·3
22	12·0	51	26·4	80	40·8	109	55·5	138	70·3	167	85·3	196	100·5	225	115·9
23	12·5	52	26·9	81	41·3	110	56·0	139	70·8	168	85·9	197	101·0	226	116·4
24	13·0	53	27·4	82	41·8	111	56·5	140	71·3	169	86·4	198	101·5	227	116·9
25	13·5	54	27·9	83	42·3	112	57·0	141	71·8	170	86·9	199	102·0	228	117·4
26	14·0	55	28·4	84	42·8	113	57·5	142	72·3	171	87·4	200	102·6	229	118·0
27	14·5	56	28·8	85	43·4	114	58·0	143	72·9	172	87·9	201	103·1	230	118·5
28	15·0	57	29·3	86	43·9	115	58·6	144	73·4	173	88·5	202	103·7	231	119·0
29	15·5	58	29·8	87	44·4	116	59·1	145	73·9	174	89·0	203	104·2	232	119·6
30	16·0	59	30·3	88	44·9	117	59·6	146	74·4	175	89·5	204	104·7	233	120·1
31	16·5	60	30·8	89	45·4	118	60·1	147	74·9	176	90·0	205	105·3	234	120·7
32	17·0	61	31·3	90	45·9	119	60·6	148	75·5	177	90·5	206	105·8	235	121·2
33	17·5	62	31·8	91	46·4	120	61·1	149	76·0	178	91·1	207	106·3	236	121·7
34	18·0	63	32·3	92	46·9	121	61·6	150	76·5	179	91·6	208	106·8	237	122·3
35	18·5	64	32·8	93	47·4	122	62·1	151	77·0	180	92·1	209	107·4	238	122·8
36	18·9	65	33·3	94	47·9	123	62·6	152	77·5	181	92·6	210	107·9	239	123·4
37	19·4	66	33·8	95	48·4	124	63·1	153	78·1	182	93·1	211	108·4	240	123·9
38	19·9	67	34·3	96	48·9	125	63·7	154	78·6	183	93·7	212	109·0	241	124·4

Table for calculating the Grape Sugar from the amount of Copper found by Gravimetric Analysis—(continued).

Copper.	Grape sugar.	Copper.	Grape sugar.	Copper.	Grape sugar.	Copper.	Grape sugar.	Copper.	Grape sugar.	Copper.	Grape sugar.	Copper.	Grape sugar.	Copper.	Grape sugar.
Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
242	125·0	270	140·0	298	155·4	326	170·9	354	186·6	382	202·5	410	218·7	438	235·1
243	125·5	271	140·6	299	156·0	327	171·4	355	187·2	383	203·1	411	219·3	439	235·7
244	126·0	272	141·1	300	156·5	328	172·0	356	187·7	384	203·7	412	219·9	440	236·3
245	126·6	273	141·7	301	157·1	329	172·5	357	188·3	385	204·3	413	220·4	441	236·9
246	127·1	274	142·2	302	157·6	330	173·1	358	188·9	386	204·8	414	221·0	442	237·5
247	127·6	275	142·8	303	158·2	331	173·7	359	189·4	387	205·4	415	221·6	443	238·1
248	128·1	276	143·3	304	158·7	332	174·2	360	190·0	388	206·0	416	222·2	444	238·7
249	128·7	277	143·9	305	159·3	333	174·8	361	190·6	389	206·5	417	222·8	445	239·3
250	129·2	278	144·4	306	159·8	334	175·3	362	191·1	390	207·1	418	223·3	446	239·8
251	129·7	279	145·0	307	160·4	335	175·9	363	191·7	391	207·7	419	223·9	447	240·4
252	130·3	280	145·5	308	160·9	336	176·5	364	192·3	392	208·3	420	224·5	448	241·0
253	130·8	281	146·1	309	161·5	337	177·0	365	192·9	393	208·8	421	225·1	449	241·6
254	131·4	282	146·6	310	162·0	338	177·6	366	193·4	394	209·4	422	225·7	450	242·2
255	131·9	283	147·2	311	162·6	339	178·1	367	194·0	395	210·0	423	226·3	451	242·8
256	132·4	284	147·7	312	163·1	340	178·7	368	194·6	396	210·6	424	226·9	452	243·4
257	133·0	285	148·3	313	163·7	341	179·3	369	195·1	397	211·2	425	227·5	453	244·0
258	133·5	286	148·8	314	164·2	342	179·8	370	195·7	398	211·7	426	228·0	454	244·6
259	134·1	287	149·4	315	164·8	343	180·4	371	196·3	399	212·3	427	228·6	455	245·2
260	134·6	288	149·9	316	165·3	344	180·9	372	196·8	400	212·9	428	229·2	456	245·7
261	135·1	289	150·5	317	165·9	345	181·5	373	197·4	401	213·5	429	229·8	457	246·3
262	135·7	290	151·0	318	166·4	346	182·1	374	198·0	402	214·1	430	230·4	458	246·9
263	136·2	291	151·6	319	167·0	347	182·6	375	198·6	403	214·6	431	231·0	459	247·5
264	136·8	292	152·1	320	167·5	348	183·2	376	199·1	404	215·2	432	231·6	460	248·1
265	137·3	293	152·7	321	168·1	349	183·7	377	199·7	405	215·8	433	232·2	461	248·7
266	137·8	294	153·2	322	168·6	350	184·3	378	200·3	406	216·4	434	232·8	462	249·3
267	138·4	295	153·8	323	169·2	351	184·9	379	200·8	407	217·0	435	233·4	463	249·9
268	138·9	296	154·3	324	169·7	352	185·4	380	201·4	408	217·5	436	233·9		
269	139·5	297	154·9	325	170·3	353	186·0	381	202·0	409	218·1	437	234·5		

In the process of gravimetrically estimating invert sugar, the details prescribed for grape sugar are followed exactly, the accompanying table being used for determining the amount of invert sugar from the copper obtained:

Table for Solutions of pure Invert Sugar.

Milligrams invert sugar.	Milligrams reduced copper.	1 milligram of invert sugar corresponds with mg. of reduced copper.	Milligrams invert sugar.	Milligrams reduced copper.	1 milligram of invert sugar corresponds with mg. of reduced copper.
50	96·0	1·876	140	259·4	1·744
55	105·4		145	268·1	
60	114·8		150	276·8	
65	124·2		155	285·2	1·684
70	133·5		160	293·6	
75	142·9		165	302·1	
80	152·1	1·840	170	310·5	
85	161·3		175	318·9	
90	170·5		180	327·2	1·656
95	179·7		185	335·5	
100	188·9		190	343·7	
105	197·8	1·772	195	352·0	
110	206·6		200	360·3	
115	215·5		205	368·2	1·592
120	224·4		210	376·2	
125	233·2		215	384·2	
130	241·9	1·744	220	392·4	
135	250·6		225	400·1	

Examples of the method of using this table:

The weight of copper = 0·1750 gram. According to the table 0·1705 Cu = 0·090 gram of invert sugar; therefore 0·1750 − 0·1705 $= 0{\cdot}0045\,\text{Cu} \times \frac{45}{1{\cdot}84}$ invert sugar = 0·0025 gram of invert sugar. Hence, 0·1750 gram Cu = 0·090 + 0·0025 = 0·0925 gram of invert sugar.

c. Estimation of Milk Sugar.

In the estimation of milk sugar, it is not, according to Soxhlet's experiments, the degree of dilution which exercises an influence on the reducing action, but the greater or smaller excess of the copper solution. The latter fact is also confirmed by Rodewald and Tollens, consequently gravimetric estimation of milk sugar must also be based upon proportions which have been fixed empirically.

The accompanying table has been prepared by Soxhlet and presupposes the carrying out of the following directions:

Twenty-five c.c. of the copper solution *a* (this vol. p. 464) and 25 c.c. of the alkaline Rochelle salt solution *b* (this vol. p. 464) is mixed with from 20 to 60 c.c. of an approximately 0·5 per cent. solution of milk sugar, and the mixture made up with water to 150 c.c. It is then heated to boiling for six minutes, the cuprous oxide collected in an asbestos filter-tube and the reduced copper weighed as in the case of grape sugar. The amount of milk sugar is then obtained from the weight of copper by completing Soxhlet's accompanying table by interpolation.

Weight of copper in milligrams.	Corresponding amount of milk sugar, in milligrams.
392·7	300
363·6	275
333·0	250
300·8	225
269·6	200
237·5	175
204·0	150
171·4	125
138·3	100

If the milk sugar in milk has to be determined, the albumin is first thrown down (also the fat) with sulphate of copper and potash solution in the manner prescribed by Ritthausen.* For this purpose, 25 c.c. of milk is diluted with 400 c.c. of water, 10 c.c. of the sulphate of copper solution mentioned in this vol. p. 464 (34·639 in 500 c.c.) is added, and then 6·5 to 7·5 c.c. of potash solution of such a strength that one volume throws down the copper from exactly one volume of the copper solution. The liquid must still have an acid reaction after the addition of the alkali and may contain some dissolved copper. After being made up to 500 c.c. and filtered through a dry folded filter, 100 c.c. of the approximated 0·25 per cent. milk sugar solution is mixed with 25 c.c. of the alkaline Rochelle salt solution and 25 c.c. of the sulphate of copper solution (this vol. p. 464) in a glass beaker, which is covered, and heated to boiling over double wire gauze. After 6 minutes boiling, it is filtered and the process carried out as described above. Assuming with Soxhlet that 0·294 gram of copper is obtained, this corresponds with 0·2236 gram of milk sugar.

d. Estimation of Maltose.

As, according to Soxhlet's researches, an excess of undiluted Fehling's solution (but only if undiluted) does not, as is the case with other sugars, increase the reducing action of maltose, and as a definite amount of maltose reduces the same amount of copper irrespective of the amount of copper which is present in excess, the gravimetric estimation of maltose is simpler than that of the other sugars, as when solutions containing approximately 1 per cent. of maltose are employed only one relation has to be considered, namely that determined by Soxhlet: 113 of copper = 100 of anhydrous maltose ($C_{12}H_{11}O_{11}$). The only point to be considered in carrying out the process is to use the Fehling's solution undiluted and in excess, this being made by mixing an equal bulk of the sulphate of copper solution *a* with the alkaline Rochelle salt solution *b* (this vol. p. 464), The liquids are mixed cold, boiled for 4 minutes and filtered (see Grape sugar).

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* Journ. f. prakt. Chem. [ii.] 15, 332.

A passing glance at the literature of the subject is sufficient to show that many other investigators besides those above referred to have worked with modifications of FEHLING's solution. The alterations in part refer to the preparation of the copper solution and partly to the manner of determining the precipitated cuprous oxide.

Concerning the first point, LÖWE's* work may be mentioned who recommends a solution of "glycerine-copper-oxide-soda;" also that of LAGRANGE,† and of DEGENER,‡ who give the preference to solutions of tartrate of copper in soda lye prepared in various ways; as well as of PAVY,§ who uses a FEHLING solution mixed with ammonia—and with reference to the latter point, those of FR. MOHR,‖ who dissolves the filtered cuprous oxide in a solution of acid ferric sulphate and determines with permanganate of potassa the amount of ferrous sulphate formed; also of W. PILLITZ,¶ who replaces the ferric sulphate by a solution of chloride of sodium in dilute sulphuric acid and oxidises the solution of cuprous oxide directly with permanganate;—of FR. WEIL,** who titrates the excess of cupric oxide remaining in solution with a stannous chloride solution (see Vol. I. p 261) estimating the precipitated cuprous oxide from the difference;—of HOLDEFLEISS,†† and of GRATAMA,‡‡ who convert the filtered cuprous oxide into cupric oxide by means of nitric acid; and of ARNOLD,§§ who dissolves the cuprous oxide in nitric acid and estimates it by VOLHARD's method (this vol. p. 396).

These modifications, however, offer no advantage, and all those which require the liquid containing the excess of FEHLING's solution to be filtered through paper, have the disadvantage that filter paper retains copper the amount of which varies with the concentration of the solution and the proportion of copper it contains.

B. Methods based upon the Reduction of Mercury Compounds.

§ 275.

Three methods are founded on this basis:

1. KNAPP'S.‖‖
2. SACHSSE'S.¶¶
3. HAGER'S.***

of which the first two have been repeatedly and critically examined, particularly by SOXHLET.†††

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* Zeitschr. f. anal. Chem. 9, 20, and 10, 452.

† Compt. rend. 1874, p. 1005; Zeitschr. f. anal. Chem. 15, 111.

‡ Zeitschr. des Vereins für Rübenzucker-Industrie, 18, 349, and 19, 736; Zeitschr. f. anal. Chem. 22, 444.

§ Chem. News, 39, 77; Zeitschr. f. anal. Chem. 19, 98.

‖ *Ibid* 12, 296.

¶ *Ibid.* 16, 48.

** *Ibid.* 11, 284.

†† Landwirtschafte. Jahrbücher, 1877, supplemental number.

‡‡ Zeitschr. f. anal. Chem. 17, 155.

§§ *Ibid.* 20, 231.

‖‖ Ann. d. Chem. u. Pharm. 154, 252; Zeitschr. f. anal. Chem. 9, 395.

¶¶ Pharmaceut. Zeitschr. f. Russland, 1876, 549; Zeitschr. f. anal. Chem. 16, 121.

*** Pharm. Centralhalle, 18, 313; Zeitschr. f. anal. Chem. 17, 380.

††† Journ. f. prakt. Chem. [ii.] 21, 300; Zeitschr. f. anal. Chem. 20, 447.

1. Knapp's Method.

This was used by Knapp, at the suggestion of Liebig, for estimating grape sugar. The requisite solution of mercury is obtained by dissolving 10 grams of pure dry cyanide of mercury in water, adding 100 c.c. of soda solution of sp. gr. 1·145, and diluting to 1000 c.c. The sugar solution employed should contain about 0·5 per cent.

As according to Brumme's observations, confirmed by Soxhlet,* the reducing effect of the sugar is greater, if the whole of the sugar is added at once, and less when added in separate portions, so Knapp's method in its original form wherein the sugar solution is added to the boiling mercury solution gradually until all the mercury is thrown down, according to Soxhlet, does not yield satisfactory results. Concordant and accurate results may be obtained, according to him, by proceeding in a way analogous to his modification of Fehling's method, that is, when the whole of the sugar (whether as 0·5 or 1 per cent. solution is almost immaterial) is added at once to the mercury solution —conveniently to 100 c.c.—and the liquid after continued boiling for 2 to 3 minutes, tested for the presence of dissolved mercury, making other trials with fresh portions of the mercury solution and larger or smaller amounts of sugar solution, until in two experiments the quantities of sugar differ but slightly, one containing just a little dissolved mercury, and the other being free from it.

For determining the amount of dissolved mercury, the reaction introduced by Sachsse is recommended; this consists in removing a few drops—or towards the end about 5 c.c.—of the liquid above the mercury precipitate, and mixing it with an alkaline solution of stannous oxide in a porcelain basin; if a large amount of mercury is present, a black precipitate is formed, whilst smaller quantities yield a brown one, or if very little is present, a brown coloration only is produced. The alkaline solution of stannous oxide is obtained by supersaturating a solution of stannous chloride with caustic soda. Haas † recommends passing the solution to be tested for mercury through a triple filter.

By operating in this way, the following relations (according to Soxhlet) obtain between Knapp's solution and the different sugars, and should be used in calculating.

100 c.c. of Knapp's solution are reduced by the following amounts of sugar, when the sugar is employed in 0·5 per cent. solution:

Grape sugar	$(C_{12}H_{12}O_{12})$ . . .	202 milligrams
Invert sugar	$(C_{12}H_{12}O_{12})$ . . .	200 ,,
Levulose	$(C_{12}H_{12}O_{12})$ . . .	198 ,,
Maltose	$(C_{12}H_{11}O_{11})$ . . .	308 ,,
Milk sugar	$(C_{12}H_{12}O_{12})$ . . .	311 ,,

However, according to Worm Müller and J. Hagen ‡ accurate results are also obtained when 0·5 to 1·0 per cent. solutions of sugar are gradually added, and this has lately been confirmed by further investigation on the part of Worm Müller § and J. G. Otto.|| They advise the following method of proceeding: For a 1 per cent. sugar solution

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* Zeitschr. f. anal. Chem. 16, 121.

† *Ibid.* 22, 216.

‡ Pflüger's Archiv. für die gesammte Physiol. 16, 569 and 590, and 23, 220.

§ Journ. f. prakt. Chem. [ii.] 26, 78.

|| *Ibid.* 26, 87.

100 c.c. of **Knapp**'s solution is taken, or for 0·5 per cent. solutions 50 c.c., diluted with 3 to 4 times its volume of water, heated to boiling, and the sugar solution added, the main bulk in portions of about 2 c.c., boiling for ½ to 1 minute between each addition. As a final reaction, W. **Müller** uses that given by **Pillitz**; **Otto**, on the other hand, the one recommended by **Lenssen**.*

Working in this way, the above-named chemists confirmed **Knapp**'s relation of reducing power, in which 100 c.c. of **Knapp**'s solution corresponds with 0·250 gram of grape sugar, and, on the other hand, **Soxhlet**'s results were confirmed when his method of working was followed.

2. R. Sachsse's Method.

An alkaline solution of iodide of mercury serves as the mercury solution; this is prepared by dissolving on the one hand 18 grams of pure and dry iodide of mercury in water, by the aid of 25 grams of iodide of potassium, and on the other an aqueous solution of 80 grams of hydrate of potassa. The latter solution is added to the former and the whole diluted to 1000 c.c. According to **Sachsse**, the sugar solution should be added in portions to the boiling mercury solution until the whole of the mercury is just precipitated. As, however, **Soxhlet** found titration by the gradual and interrupted addition of sugar yielded results which were different from those obtained when the sugar solution was added all at once, it is necessary in order to obtain exact results to adopt the same method of procedure when using **Sachsse**'s solution, as **Soxhlet** prescribes for **Knapp**'s solution of mercury.

It is worthy of note that there is a difference between the effects of gradual, as compared with complete, addition of the sugar solution, in **Knapp**'s and **Sachsse**'s methods. In the former, if the sugar solution is gradually added, more sugar is required to effect reduction, and with the latter less. This has of course to be considered in determining, from the preliminary test, the amount of sugar solution with which it is advisable to commence the actual experiment.

In carrying out **Sachsse**'s method, it must moreover be borne in mind that the reducing effect of a 1 per cent. solution is different from that of a 0·5 per cent. solution. The 0·5 per cent. degree of concentration must on that account not be appreciably departed from.

In working, 100 c.c. of **Sachsse**'s solution is a convenient quantity, the boiling being continued 2 to 3 minutes, the presence or otherwise of dissolved mercury in the solution being tested for by an alkaline solution of stannous oxide.

The relation between **Sachsse**'s solution and the different sorts of sugar under these conditions has been determined by **Soxhlet** as follows:

100 c.c. of **Sachsse**'s solution are reduced by the following amounts of sugar, when 0·5 per cent. solutions are used:

Grape sugar	($C_{12}H_{12}O_{12}$)	325	milligrams
Invert sugar	($C_{12}H_{12}O_{12}$)	269	„
Levulose	($C_{12}H_{12}O_{12}$)	213	„
Maltose	($C_{12}H_{11}O_{11}$)	491	„
Milk sugar	($C_{12}H_{12}O_{12}$)	387	„

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* Zeitschr. f. anal. Chem. 9, 455. **Lenssen** acidifies a filtered sample with acetic acid and tests for mercury by sulphuretted hydrogen.

With reference to both these methods based on the precipitation of mercury, it should be noted that the values arrived at by SOXHLET are naturally for sugar in a perfectly pure condition. With such, the same results will be obtained by using the empirically derived values under the given conditions, whether FEHLING'S, KNAPP'S, or SACHSSE'S method, as modified by SOXHLET, is employed. The case is otherwise, however, if the different methods are employed on sugar solutions in which—as for example in the case of commercial grape sugar—products intermediate between dextrin and grape sugar, or—as in wine extract—glycerin are present, as both the latter and also the intermediate starch products reduce the mercury solutions (at least HAAS found this to be the case with SACHSSE'S solution), but not FEHLING'S copper solution.* On this account, SACHSSE'S method when employed for such impure sugar solutions (and in all probability the same is true of KNAPP'S method) yields results which are too high. The use of SOXHLET'S modification of FEHLING'S method is therefore decidedly preferable for estimating the sugar in such cases.

3. H. HAGER'S Gravimetric Method.

This up to the present time has only been proposed to be used for determining grape sugar, and as far as the author is aware has not yet been tested for other sugars.

The following solution serves as the reagent: 30 grams of oxide of mercury is ground up with 30 grams of acetate of soda, transferred to a flask, and 25 grams of concentrated acetic acid (or 100 c.c. of dilute acetic acid of sp. gr. 1·04) is added, and then 50 grams of chloride of sodium and sufficient warm water to make up about 1000 c.c.; shaking and warming gently assist solution.

After cooling, the liquid is filtered and kept in a cool place protected from light.

For estimating the sugar, the sugar solution together with an excess of the mercury solution (about 200 c.c. of the mercury solution to 1 gram of grape sugar) is placed in a flask provided with a perforated cork in which is fixed a glass tube about 15 cm. long, and heated either on a water bath or over a naked flame for one to two hours, care being taken that the liquid always remains acid. In proportion as the sugar acts, mercurous chloride separates. The reaction is completed when a small portion of the clear liquid becomes turbid on the addition of ammonia, showing that acetate of mercury is still present, whilst the filtered liquid remains clear on further boiling. The mercurous chloride is collected on a tared filter which has been dried at 100°, and is washed first with 5 per cent. hydrochloric acid, then with water, and finally with spirits of wine, dried in a water oven and weighed. As according to HAGER 2 equiv. of grape sugar = 360, decompose 18 equiv. of oxide of mercury = 1944 and yield 9 equiv. of mercurous chloride = 2119·14, therefore 5·886 grams of the latter correspond with 1 gram of grape sugar, $C_{12}H_{12}O_{12}$.

The acid solution of acetate of mercury containing chloride of sodium has no action on cane sugar, glycerine, gum arabic, dextrin or uric acid, but as it acts on other constituents of urine, the process is not available for the estimation of sugar in diabetic urine.

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* According to HAAS, 2·1618 grams of glycerin reduce 20 c.c. of SACHSSE'S mercury solution.

C. Method based upon the Decomposition of Sugar by Alcoholic Fermentation.*

§ 276.

1. When a liquid containing grape sugar is exposed to the proper temperature along with ferment or yeast, it undergoes alcoholic fermentation. It was formerly supposed that 1 equiv. of anhydrous grape sugar gave 2 equiv. of alcohol and 4 of carbonic acid, as represented by the equation,

$$C_{12}H_{12}O_{12} = 2\,C_4H_6O_2 + 4\,CO_2.$$

In accordance with this assumption, 48·89 parts of carbonic acid would correspond with 100 parts of anhydrous grape sugar, but Pasteur has shown † that this assumption is incorrect, as during alcoholic fermentation a variety of other products are formed from the elements of the sugar, especially glycerin, succinic acid, cellulose, and fats, besides certain compounds, the formation of which was already known, but which occur only in very small quantities, such as amylic and butylic alcohols, &c. If, therefore, the quantity of sugar decomposed is to be estimated from the amount of carbonic acid evolved during the alcoholic fermentation, the calculation must be founded on the practical results of experiments. As, however, the total amount of the several bye-products is by no means constant, it is obvious that the method for estimating sugar based on the amount of carbonic acid evolved during fermentation cannot lay claim to absolute accuracy. From Pasteur's experiments (*loc. cit.*), it appears that out of 100 parts of grape sugar only about 95 parts are decomposed into alcohol and carbonic acid, as indicated by the above equation, the remainder being decomposed into 2·5—3·6 of glycerin, 0·4—0·7 of succinic acid, 0·6—0·7 of carbonic acid, and 1·2—1·5 of cellulose, fat, and other undetermined products. Consequently we shall not depart far from the truth if we reckon that 47 parts of carbonic acid obtained by alcoholic fermentation represent 100 parts of anhydrous grape sugar.

2. To determine the carbonic acid evolved during fermentation, the apparatus figured in Vol. I. p. 344, Fig. 94 is used, omitting the sulphate of copper pumice tube *l*, and taking care that the tubes *n* and *o* contain sufficient soda-lime to absorb all the carbonic acid which may be evolved. If the carbonic acid is to be estimated by the loss of weight of the apparatus, the one represented in Fig. 90, Vol. I. p. 339, should be employed, substituting for the flask *B* a U-tube filled with pumice moistened with sulphuric acid; the quantity of sulphuric acid should be so adjusted that the bend of the tube may be just closed by the liquid. The exit of the U-tube is connected with a chloride of calcium tube (this is not weighed), so that the sulphuric acid in the U-tube may not absorb moisture from the air.

3. The experiment is made with a quantity of the saccharine liquid containing about 2 or 3 grams of anhydrous sugar. If much more is taken, the fermentation lasts too long; if, on the other hand, much less is used—at least, when the carbonic acid is estimated by the loss of

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* Compare Krocker, Bestimmung des Stärkemehlgehaltes in vegetabilischen Nahrungsmitteln, Ann. d. Chem. u. Pharm., 58, 212.

† Compt. rend., 48, 1149; Jour. f. prakt. Chem. 85, 465.

weight of the apparatus—the results are inaccurate, as the quantity of the carbonic acid evolved is too small.

4. As regards the concentration of the liquid, the solution should contain about 4 or 5 parts of water to 1 of sugar; solutions which are dilute must therefore be concentrated by evaporation on the water-bath.

5. The sugar solution is poured into the flask, a few drops of solution of tartaric acid added, and also a comparatively large, weighed portion of washed yeast, say 20 grams of fresh, or a corresponding quantity of pressed yeast. As yeast generally evolves some carbonic acid, an experiment may be made at the same time with a larger quantity of the same yeast in a similar apparatus, so as to determine the amount of carbonic acid it evolves; in this way a correction can be made for the 20 grams of yeast used in the experiment.

6. When the apparatus has been arranged and the weighing made, the apparatus, or the flask containing the sugar solution and yeast, as the case may be, is put in a place where the temperature remains tolerably constant at 25°. Fermentation soon sets in, and goes on briskly as first, but after a time more and more slowly. In about 4 or 5 days, when no more gas bubbles are formed, the process will be completed. The fermentation flask is now heated to 100° and the remaining carbonic acid sucked out of the apparatus, after which it is allowed to cool, and then weighed. The increase in weight of the carbonic acid apparatus, or the loss in weight of the fermentation apparatus and drying tube, represents the carbonic acid evolved. Every 47 parts of the latter, as shown above (1), correspond with 100 parts of anhydrous grape sugar.

D. Estimation of Cane Sugar, Dextrin and Starch.

§ 277.

1. Cane Sugar.

Cane sugar is generally estimated optically or aræometrically, see this vol. p. 459.* Of other methods, the inversion method is particularly suitable, and also, in many cases, the fermentation method.

a. Inversion.—This as a rule is most simply carried out by heating the cane sugar with very dilute hydrochloric acid. The most favourable proportions were ascertained by Nicol † and in the main confirmed by Soxhlet.‡ Nicol recommends dissolving 1·25 grams of sugar in a 250 c.c. litre flask in 200 c.c. of water, adding 10 drops of hydrochloric acid of sp. gr. 1·11, and heating at 100° for half an hour in a water bath. The solution is then neutralised with carbonate of soda, the flask filled up to the mark with water, and the liquid well mixed. If the heating is continued longer, a part, although only a small one, of the invert sugar formed is decomposed, thus slightly lowering the reducing power of the solution. According to Soxhlet, for example, the proportion resulting from heating for 1½ hours is as 100 : 99·3.* He recommends the following proportions for the purpose of inversion, which, if pure and dry cane sugar is used, will yield a solution of invert sugar containing exactly 1 gram or 0·5 gram of invert sugar in 100 c.c. : 9·5 grams of cane sugar is dissolved in 700 c.c. of hot water, 100 c.c. of N/5 hydrochloric acid (containing 0·729 of hydrogen chloride) is added, the mixture heated for 30 minutes at 100° in a water bath, neutralised exactly with titrated soda solution, and made up to 1000 or 2000 c.c. as the case may be. In the solution obtained by one of these two methods, the invert sugar is determined either by Soxhlet's volumetric or Meissl's gravimetric method, see this vol. pp. 464 and 467, reckoning 95 parts of cane sugar ($C_{12}H_{11}O_{11}$) for every 100 parts of invert sugar ($C_{12}H_{12}O_{12}$).

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* With respect to the optical estimation of cane sugar in presence of other sugars or carbohydrates, see Clerget (Annales de chim. et de phys. [iii.] 26, 175); H. Reichardt and C. Bittmann (Zeitschr. des Vereins f. d. Rübenzuckerindustrie, 1882, 764); S. Casamajor (Chem. News, 45, 150); K. Zulkowsky (Ber. der œsterr. Gesellsch. zur Förderung der Chem. Industrie, ii. 1883); Kjeldahl (Meddelelser fra Carlsberg Laboratoriet, pt. 3, Copenhagen, H. Hagerup); also Zeitschr. f. anal. Chem. 22, 588, pt. 4.

† Zeitschr. f. anal. Chem. 14, 177.

‡ Journ. f. prakt. Chem. [ii.] 21, 228.

If the method is applied to the estimation of the sugar in *beet-juice*, the aqueous extract of the pressed residue after extraction, &c., acetate of lead is first added to the weighed or measured quantity, until a precipitate is no longer produced, the excess of lead, after filtering, is thrown down by a sufficient quantity of sulphate of soda, and the solution inverted by heating with hydrochloric acid.

If it is to be feared that other substances present in the solution along with the cane sugar may, when heated with hydrochloric acid, be converted into products capable of reducing Fehling's solution, as for instance, dextrin into grape sugar, the inversion should be effected by Kjeldahl's † method with invertin (the inverting ferment of yeast).

The invertin is used either in the form of an aqueous extract of the previously well washed yeast, or as a mixture of washed yeast with a little alcoholic solution of thymol, the addition of which completely paralyses the fermenting power of the yeast, whilst it has no influence on the invertin.

Invertin changes cane sugar easily and completely into invert sugar without acting on most of the other carbohydrates; ‡ the most favourable temperature being between 52° and 56°. The presence of salts of the alkalies hinders the action of the invertin, but *small quantities* of acids increase it.

If it is a question of determining *cane sugar in the presence of grape sugar*, the latter is ascertained by Soxhlet's volumetric method (this vol. p. 464) in one part of the solution. An equal quantity of the solution is then inverted as above by heating with hydrochloric acid, or by means of invertin; in this portion there is now the invert sugar from the cane sugar along with the unaltered grape sugar. The amount of Fehling's copper solution reduced by the solution of the mixed sugars is ascertained according to Soxhlet's method, the quantity referable to the grape sugar is deducted, and the difference gives the amount corresponding with the invert sugar. Finally 95 parts of cane sugar are reckoned for each 100 parts of the invert sugar thus found.

In a similar manner, *cane sugar may also be estimated in the presence*

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* Journ. f. prakt. Chem. [ii.] 21, 235.

† Meddelelser fra Carlsberg Laboratoriet, Copenhagen (H. Hagerup 1881), p. 339, respect. p. 189; Zeitschr. f. anal. Chem. 22, 588.

‡ With the exception of a few rare sugars, synanthrose is the only one which is changed by invertin.

of invert sugar. Kjeldahl (*loc. cit.*), employing inversion with invertin, estimates cane sugar in this manner, not only in presence of grape sugar and invert sugar, but also when is it associated with maltose, dextrin and inulin.

This method presupposes that the presence of cane sugar is without effect on the reducing action of grape sugar and invert sugar, an assumption acquiesced in by Soxhlet in view of the short time the boiling continues in his process for estimating sugar, but according to Meissl's investigations this assumption is not absolutely correct. At any rate it only holds good for Soxhlet's method, but in no way for the gravimetric processes for estimating either grape sugar or invert sugar. However, to render a gravimetric estimation of invert sugar in presence of cane sugar possible, Meissl[*] has prepared a special table in which allowance is made for the influence of the cane sugar. This table has subsequently been enlarged by Zulkowsky.[†]

b. Fermentation Method.—The method, described in this vol. p. 476, for estimating sugar by the amount of carbonic acid evolved during alcoholic fermentation, is also available for cane sugar. The fermentation of the latter is more difficult than that of grape sugar, and consequently a larger quantity of yeast must be used.

This acts by the ferment contained in it, that is the invertin, first inverting the cane sugar, then the dextrose ferments, and later on the levulose. The products formed in the fermentation of cane sugar are the same as in the case of grape sugar. For each 49 parts of carbonic acid, 100 parts of cane sugar must be reckoned. The figure 49 is the average of the values 48·889 and 49·20 directly determined by Balling and by Pasteur.

2. Dextrin and Starch.

Of the different methods which can be used for the estimation of dextrin and starch, only those based upon the conversion of these compounds into grape sugar will be treated of here. Formerly the change was effected by means of sulphuric acid in pressure flasks in a salt bath (Musculus) or in sealed tubes (Pillitz).[‡]

The object is however more easily and completely accomplished by heating with hydrochloric acid; for this purpose R. Sachsse[§] recommends the following method: 2·5 to 3 grams of starch is heated in a flask with 200 c.c. of water and 20 c.c. of hydrochloric acid of sp. gr. 1·125, for three hours in a water bath kept boiling briskly, using a reflux condenser. The conversion is then, according to Sachsse, complete; that is, no change in the proportions whether of water, acid, time, or heat will produce more dextrose from a given amount of starch than can be obtained by adhering to the above rules. When the heating is finished, the solution is filtered, almost completely neutralised with soda solution (alkalinity must be avoided), diluted to 500 c.c., and the grape sugar formed is estimated volumetrically or gravimetrically, calculating 990 parts by weight of starch for each 1080 parts of grape sugar or 91·67 parts per 100. These proportions obtained by SACHSSE in his experiments with potato starch correspond with the formula $C_{36}H_{31}O_{31}$ established by W. NÄGELI instead of with the generally accepted formula for starch, $C_{12}H_{10}O_{10}$. If the calculation is based upon the ordinary formula for starch, then 90 parts of starch must be calculated for each 100 of grape sugar, that is the same proportion as in the calculation of the amount of dextrin from the grape sugar found.

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[*] Zeitschr. des Vereins f. Rübenzuckerindustrie, 1879, p. 1034.

[†] Bericht der österreich. Gesellsch. zur Förderung der Chemisch. Industr. ii. 1883.

[‡] Zeitschr. f. anal. Chem. 11, 57. See also the extended investigation by Allihn (Journ. f. prakt. Chem. [ii.] 22, 84, *et seq.*; according to him, under the most favourable conditions (0·5 per cent. sulphuric acid at 108°), only 94·5 per cent. of the starch are converted into sugar in 14 hours.

[§] Chem. Centralbl. 1877, 732; Zeitschr. f. anal. Chem. 17, 231.

On employing SACHSSE's inversion process for potato starch dried at 120° and estimating the grape sugar produced by ALLIHN's method, SALOMON * found that the amount of grape sugar (100 parts grape sugar equivalent to 90 parts starch) corresponded with the generally accepted starch formula $C_{12}H_{10}O_{10}$, and attributed the variation in SACHSSE's results partly to an insufficient dehydration of the starch (drying only at 100–110°) and partly to the manner of estimating the sugar.

Whilst formerly it was assumed that the behaviour of starch from different plants when heated with acids was identical, and that equal weights of starch from whatever source, produced the same quantity of grape sugar, it must now be acknowledged, if the work of SACHSSE and SALOMON † are accepted as conclusive and comparative, that this is not the case, at least with the starches occurring in commerce; they found that on treating rice starch and wheat starch, a smaller amount of grape sugar was formed than from an equal quantity of potato starch.

The question whether the starches in different plants exhibit differences in behaviour is not yet thereby decided, as the variations in commercial starches may be due to their mode of preparation. SALOMON assumes, on the basis of his researches, that the difference referred to is due to a part of the starch in certain kinds, such as rice starch, although it is completely dissolved on heating with dilute acids, being nevertheless converted, not into grape sugar, but into other compounds which do not reduce FEHLING's solution. SALOMON's figures for rice starch show that 93·50 of starch correspond with 100 parts of grape sugar produced.

For wheat starch, L. SCHULZE ‡ recently found the relationship to be 100 of grape sugar = 90 of starch. The author considers, therefore, that the question is not yet settled for rice starch.

By employing the foregoing methods of estimating starch in grain, the results, according to G. FRANCKE,§ are too high, as cellulose is also converted into sugar on heating with hydrochloric acid. Treating the starch with malt infusion (diastase) at temperatures up to 65°, easily brings about a complete solution of the starch, but effects a complete conversion into maltose only very slowly, if at all. The solution always contains dextrin, or more precisely different dextrins, along with the maltose, the proportion varying with the temperature at which the diastase acts (O'SULLIVAN).|| If, however, it is desired to make a direct estimation of starch on this basis, one of the following more recently introduced methods may be adopted.

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* Repertor. d. analyt. Chem. 1, 274, and Journ. f. prakt. Chem. [ii.] 25, 348; Zeitschr. f. anal. Chem. 22, 111.

† Journ. f. prakt. Chem. [ii.] 26, 324; Zeitschr. f. anal. Chem. 22, 594.

‡ Journ. f. prakt. Chem. [ii.] 28, 311.

§ Zeitschr. f. Spiritusindustr. 1882, 306; Ber. deutsch. chem. Gesell. 16, 976.

|| Journ. Chem. Soc. Trans. 1872, 579; Trans. 1876, i. 478; and ii. 125.

a. Faulenbach* employs the following solution of diastase: a mixture of 2 litres of water and 4 litres of glycerine is poured on to 3·5 kilos of fresh green malt previously crushed, and the mixture allowed to stand eight days with occasional stirring; it is then pressed and the liquid filtered. Five drops of the liquid thus prepared dissolve 1 gram of starch, and every 15 drops contain an amount of carbohydrates corresponding with 1 milligram of grape sugar. The solution keeps well. In testing a feeding stuff, in which about 2 grams of starch should be present, the starch is gelatinised, and the solution brought about with the aid of 15 drops of the diastase solution (by digesting at about 63°). The liquid filtered from the residue of undissolved cellulose, &c., is first heated for three hours in a water-bath, with 20 c.c. of hydrochloric acid, then made exactly neutral with caustic soda, and the grape sugar determined in it; 1 milligram is deducted, and the starch calculated from the sugar.

b. O'Sullivan† employs pure diastase,‡ and in estimating starch in corn treats 5 grams of the finely ground substance successively with ether, with alcohol at 35° to 40°, and with water (at the same temperature), so as to remove fat, sugar, soluble albuminates and soluble carbohydrates. The residue is then boiled for a few minutes with 40 to 45 c.c. of water in order to gelatinise the starch, allowed to cool down to 62° or 63°, and 0·025 to 0·035 grams of diastase dissolved in a little water is added, keeping the whole at 62–63° for an hour. The liquid is then heated to boiling, filtered, and washed with hot water; the filtrate when cold is made up to 100 c.c., the maltose in it is estimated (§ 274) on the one hand, and on the other the dextrin by polarisation, deducting from the total polarisation that which is due to the effect of maltose. Both maltose and dextrin are then calculated to starch, and the amounts added together.

II. Estimation of Alcohol.

§ 278.

The estimation of alcohol (ethyl alcohol) in mixtures of alcohol and water is almost exclusively effected by areometry, either by the employment of an alcoholometer from which the percentage, by weight or volume, of alcohol can be read off direct, or by using an ordinary areometer and calculating the percentage of alcohol from the specific gravity, a large number of tables having been published which offer every facility for this purpose. The tables calculated by O. Hehner,§ and based on Fownes' tables, which, however, only gave the percentage in whole numbers, are very convenient for this purpose; these give complete volume and weight percentage.

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* Zeitschr. f. physiol. Chem. 7, 510; Chem. Centralbl. 1883, p. 632.

† Journ. Chem. Soc. Trans. 1884, p. 1.

‡ This is prepared as follows: Enough water is poured on to 2 or 3 kilos of finely-bruised pale barley malt so as just to cover it. After three or four hours it is pressed, the solution filtered, and spirits of wine of sp. gr. 0·83 added to the clear liquid until the liquid above the flocculent precipitate becomes opalescent or milky. The precipitate is collected and washed, first with spirits of wine of sp. gr. 0·86 to 0·88, then with absolute alcohol, pressed between linen, and dried completely in a vacuum over sulphuric acid.

§ Zeitschr. f. anal. Chem., 19, 485. The tables are published separately by C. W. Kreidel, Wiesbaden, 1881; English edition, J. & A. Churchill, London, 1880.

There is no occasion to dilate on this simple method of alcohol estimation, nor on the use of the vaporimeter, the utility of the results obtained from this depending entirely on the proper adjustment of the instrument.* In the following, only the process of alcoholic determination used in the analysis of wines and other liquids produced by alcoholic fermentation is described. It will readily be seen that the process employed, and which has long been in use in the author's laboratory, is quite independent of the accuracy of special apparatus.

The principle of the method is well known. The alcoholic liquid is distilled until all the alcohol has passed over with the distillate, taking care that the latter contains no appreciable quantity of any other volatile substance; the absolute weight and specific gravity of the distillate are taken, and from these data, by means of the alcohol tables, the amount of alcohol in the distillate is calculated, and from this that in the original liquid.

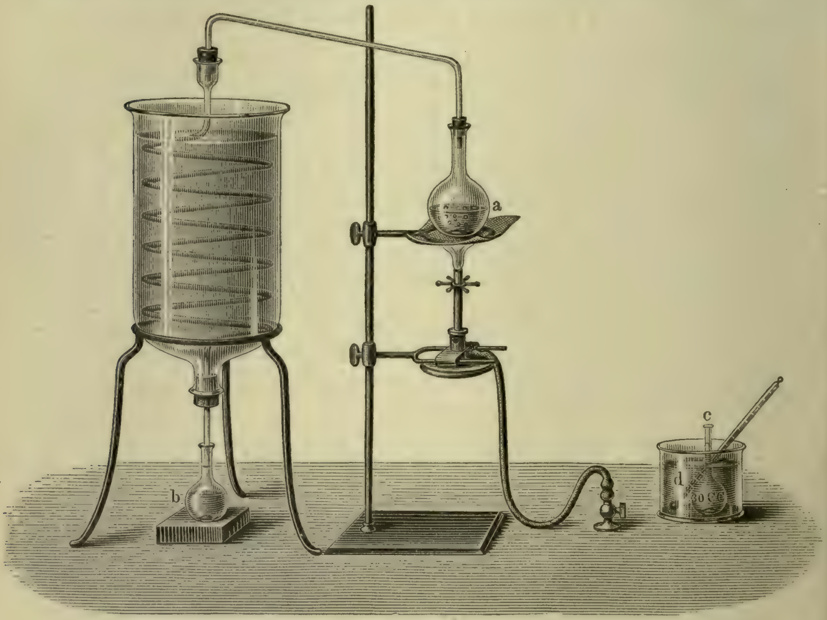

Fig. 125.

Many different forms of apparatus can of course be employed for the distillation. The apparatus, shown in Fig. 125, which does not require further description, can, however, be recommended as very convenient, as it takes up but little room, and does not require renewal of the condensing water.†

If a large quantity of the alcoholic liquid under examination, which presumably does not contain more than 20 per cent. by volume of alcohol, is available, 150 c.c. or grams is placed in the small distilling flask *a*, a little tannin being added to wines, &c., to prevent frothing, and distilled, the distillate being collected in a weighed or tared flask *b*, having a capacity, up to the mark on the neck, of about 100 c.c., that is, about two-thirds of the liquid taken. As soon as the distillate has reached up to the mark on the neck, it may safely be assumed that all the alcohol will have passed over with the distillate. The flask *b*, with its contents, is now weighed, and the absolute weight of the latter thus ascertained.

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* Compare A. Kraft, Zeitschr. f. anal. Chem. 12, 50, and A. Salomon, Annal d. Œnologie, 1, 374.

† An apparatus admitting of the distillation of several samples of wine at the same time has been described by B. Landmann (Zeitschr. f. anal. Chem. 22, 394).

For estimating the specific gravity of the distillate, which can of course only be done *after thoroughly mixing*, a pyknometer, holding 25 to 60 c.c. is employed, similar to that shown at *c* in Fig. 125. The neck of this vessel should have a diameter of 5 to 6 millimetres. Its weight,* *a*, and the number of grams of distilled water, *b*, that it will contain at 15·5°, have been previously ascertained by repeated experiments. The pyknometer is filled with the distillate to a little above the mark by means of a funnel with a finely drawn out neck, and placed in water at 15·5°, see Fig. 125, *d*. As soon as it is certain that the contents of the pyknometer have attained the same temperature as the surrounding water, as much of the distillate is withdrawn by the aid of a strip of blotting paper as will leave the flask full exactly to the mark; it is then dried and weighed. By dividing the weight of the distillate in the flask by the known weight of the distilled water it will contain at 15·5°, the sp. gr. of the distillate is obtained, and from this the amount of alcohol in the distillate and consequently in the liquid distilled, can be ascertained by the aid of Hehner's tables above mentioned.

If there is only a limited quantity of the liquid to be tested, only 50 c.c. or grams of it is distilled. The mark on the flask *b* must then register a content of 35 c.c. or so, and as a matter of course a pyknometer holding 25 to 30 c.c. must be taken, or the distillate before weighing must be made up with sufficient water to fill one of larger size.

An example will serve as explanation. 150 c.c. of wine yielded 102·0 grams of distillate of 0·9809 sp. gr. at 15·5°. Hence (according to Hehner's tables) 100 grams of the distillate contain 12·46 grams of absolute alcohol. If, therefore, 100 grams contain 12·46 grams, 102 grams will contain 12·709 grams, and as the whole of the alcohol passed over into the distillate, the latter number represents the amount in the 150 c.c. of wine, but as 150 c.c. contain 12·709 grams, 100 c.c. will contain 8·47 grams. If it is also desired to ascertain how many grams of alcohol are present in 100 grams of wine, then the sp. gr. of the latter must be determined, to find out how many grams 100 c.c. will weigh.

When it is a question of determining the amount of alcohol present in liquids containing a comparatively small amount, the distillate is collected in an unweighed flask. As soon as all the alcohol has passed over, the distillate is re-distilled and the absolute and specific weights of alcohol ascertained from the second distillate, as above.

In the case of liquids which are so thick that direct distillation is attended with difficulties, it is advisable to effect the first distillation by steam (see this vol. p. 249, *b.*), the distillate being again redistilled as above. E. BORGMANN[*] makes use of this process with the best results for the estimation of small amounts of alcohol in American malt extracts.

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* To dry such a pyknometer, it is heated and the moist air sucked out by means of a narrow glass tube. The neck may be finally dried by filter-paper.

If the liquids to be distilled contain much free carbonic acid, as is the case with new or sparkling wines, or beer, the greater part of this gas must be first removed by shaking in a half-filled flask, then adding a little milk of lime until the liquid is just alkaline, and distilling at once. This last named addition is also made when the liquid under examination contains any appreciable quantities of acetic acid or other volatile acid. In distilling with the addition of milk of lime, the presence of ammonia in the distillate, which is certain to occur if the liquid distilled contains any ammoniacal salts, must be guarded against. If any is found in the distillate, it must be removed by adding an aqueous solution of tartaric acid until the liquid is acid, and then rectifying.

III. ESTIMATION OF TANNIN.

The estimation of tannin in oak-bark and other tanning materials, in extracts containing tannic acid, as also in commercial tannic acid, is of such frequent occurrence in chemical laboratories that a description of the methods employed for this purpose naturally finds a place here. From the numerous methods which have been proposed with this object, those only will be chosen which have proved the most trustworthy.

A. LÖWENTHAL'S Method.[†]

§ 279.

This process is based upon the oxidation of the tannic acid, in sulphuric acid solution, by a solution of permanganate of potassa (formerly chloride of lime was used) in presence of a considerable quantity of solution of indigo-carmine. If the liquid is properly diluted, the oxidations are perfectly normal,[‡] and if the indigo solution has been added in such quantity as to require about twice as much of the oxidizing agent as the tannic acid, one may be quite sure that the last particle of tannic acid is oxidized with the last trace of indigo.

At first [§] it was assumed, with LÖWENTHAL, that of the substances contained in tannin extract the tannic acid alone is oxidized, but it was very soon ascertained that certain other substances passing into solution, which for the sake of brevity may be called "other substances," use up an appreciable quantity of the permanganate of potassa.[||] NEUBAUER,[¶] therefore, modified the process by estimating, on the one hand, the total quantity of tannic acid plus the "other substances," whilst, on the other, he determined the "other substances," after the tannic acid had been precipitated by animal charcoal, calculating the amount of tannic acid by difference. LÖWENTHAL,[**] on further investigating the process, retained the principle on which NEUBAUER worked, but in place of animal charcoal used, for precipitating the tannic acid, a solution of glue containing much chloride of sodium, or by HAMMER's so-called "Blösse"—animal hide prepared for tanning and reduced to powder (see Method B). As he gave the preference to the glue, the improved LÖWENTHAL method was almost exclusively practised with gelatin solution.

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[*] Zeitschr. f. anal. Chem. 22, 534.

[†] This in its earliest form is described in Journ. f. prakt. Chem. 1860, 3, 150.

[‡] See Fr. GAUHE, Zeitschr. f. anal. Chem. 3, 123.

[§] Journ. f. prakt. Chem. 1860, 150; Zeitschr. f. anal. Chem. 3, 122.

[||] Compare Fr. GAUHE, Zeitschr. f. anal. Chem. 3, 125.

[¶] Zeitschr. f. anal. Chem. 10, 1.

[**] *Ibid.* 16, 33, and 201; also 20, 91.

After SIEMAND * had found, however, that the improved LÖWENTHAL method yielded concordant results when the degree of concentration was the same, but that the results differed widely as the concentration varied owing to a slight solubility of the gelatin tannate, he showed that the process could be further improved by determining the amount of permanganate required for the dissolved gelatin tannate, and deducting this from the total amount needed for the "other substances" together with the dissolved gelatin tannate.

As, however, these corrections, whose value must be experimentally determined for varying dilutions in each case, make the method more cumbersome, SIEMAND finally reverted to HAMMER's principle, already applied by LÖWENTHAL, of removing the tannic acid by means of a solid substance which would combine with it. Experiments for ascertaining the most suitable substance for this purpose finally showed that the glue yielding tissue of bone or the so-called "Horn-schläuche" is preferable to the "Blösse" (prepared hide) proposed by HAMMER and applied by LÖWENTHAL, in so far that the former is easier to prepare, gives up less soluble matter on digestion with water,† and effects the precipitation of the tannic acid more rapidly.

LÖWENTHAL's method, as the result of these improvements, gained considerably in trustworthiness over its original form, and consequently the newest and best modification is alone described in detail here.

I. REQUISITES.

To carry out this method the following are required :

1. A solution of permanganate of potassa.—For this purpose 1 gram of the pure salt is dissolved in water and made up to 1 litre.

2. Indigo-carmine solution.—40 grams of purest indigo-carmine paste are dissolved in water, 60 c.c. of sulphuric acid added, the whole made up to 1 litre with water, and filtered.

3. Glue-yielding tissue of bones, or horn cartilage.—*a.* The former is prepared according to SIEMAND's directions, in the following manner: Hollow bones from which the ends and marrow have been removed, are broken into large pieces and after being digested for two days with a 5 per cent. solution of soda, are brushed and washed repeatedly with water, leaving them each time for a few hours in contact with the water. The bones are then broken into pieces the size of a nut and treated with dilute hydrochloric acid, containing 1 litre of crude hydrochloric acid in each 8 litres, until they become

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* Dingler's Polyt. Journ. 244, 390 ; Zeitschr. f. anal. Chem. 22, 595.

† SIEMAND obtained from each 10 grams of the substance, by 48 hours' treatment with 200 c.c. of water and evaporating, the following residues from every 100 c.c. of the filtrate : From Blösse (prepared hide), 0·25 ; from extracted bones, 0·008 ; and from Hornschläuche (or horn cartilage), 0·004 grams. The aqueous solutions of all three substances, however, were free from any substance appreciably oxidisable by permanganate.

soft. They are now nearly freed from acid by water and run while *moist* through a small mill.[*] The pulpy mass is then digested frequently with a more dilute hydrochloric acid (1 : 20) to remove the last traces of lime salts, as well as ferric oxide, and finally well washed, first with rain or spring water until no longer acid, and then with distilled water, pressed and dried. It is preferable to divide the preparation by sieving, using each size separately.

b. Horn cartilage (the bony, vascular quick of cow horn).—This is freed from salts of lime in exactly the same way as the bone-preparation. The preparation when softened by water has a cartilaginous appearance.

Instead of these substances—as has been already remarked—hide prepared for tanning may be used, but the former are preferable. The prepared hide is best obtained from a tannery; for the further treatment see below, under method B.

II. PROCESS.

1. An aqueous solution of the tanning material suitable for tannin estimation is prepared, taking care to employ as much of the substance, whose tanning principle is to be brought into solution, as will be sufficient to yield a solution containing 0·5 to 1·0 gram of tanning principle per litre.

With this object, the following quantities of the substances mentioned should be taken:

Pine bark	about	10 to 15 grams.
Oak bark	,,	8 to 10 ,,
Spanish chestnut wood	,,	6 to 8 ,,
Valonia	,,	3 to 4 ,,
Sumach	,,	6 to 8 ,,

The finely divided vegetable substance is extracted by boiling with water at least four times and the liquid made up to 1 litre. With wood, such as for example, that of the Spanish chestnut, each boiling should last for fifteen minutes as a minimum, wood being more difficult to extract.

In the case of extracts whose content of tanning matter is as a rule approximately known, the amount to be dissolved for the production of 1 litre of liquid of the above-named degree of concentration, can be easily estimated.

If the extracts are clear, or clarify on standing, they can be at once used for examination, otherwise a sufficient quantity must be passed through a dry filter. If turbid extracts are used, somewhat higher results are obtained, but these are inaccurate, as the suspended organic matter also uses up permanganate of potassa.[†]

Should the extract contain pectinous compounds, these must be removed to ensure correct results, because—as JULIUS LÖWE[‡] first pointed out—these are also thrown down by the tannin precipitating preparations (particularly hide powder, and also by the bone, and horn cartilage). For this purpose, according to Löwe, the extracts, for example those of oak bark which always contain pectinous substances, are evaporated to dryness on the water bath with a drop of acetic acid, the residues extracted with strong spirits of wine (which dissolves the tannic acid and leaves the pectinous substances), the alcoholic solution again evaporated on a water bath until the alcohol is completely removed, and the residue then taken up with water.

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[*] According to experiments in the author's laboratory, the object is better accomplished by grinding the dry preparation.

[†] In experiments conducted in the author's laboratory, the following results, as examples, were obtained: With an oak bark extract, employing the filtered solution, 26·04, against 27·52 per cent. oak tannin with the unfiltered solution. With an extract containing tannin, the filtered solution gave 12·53, and the unfiltered 13·66 per cent. tannin.

[‡] Zeitschr. f. anal. Chem. 4, 368.

2. The effective value of the solution of permanganate of potassa is determined by iron or oxalic acid, see Vol. I. pp. 215 and 217.

3. Twenty c.c. of the indigo solution is measured out, 1 litre of water added, and the beaker containing the liquid is placed in a white porcelain basin; then—most conveniently from a burette with a glass tap—the permanganate of potassa is run into the solution drop by drop in about four minutes, stirring continuously. The deep blue solution gradually turns dark green, then light green, assuming later a yellowish green tint from which the next drop of permanganate causes the last greenish tinge to disappear. In order to sharply distinguish the end reaction, it is necessary towards the end to add the permanganate of potassa solution very slowly in single drops. If the change from the yellowish green tint to pure yellow is not sharp, the indigo-carmine is not sufficiently pure, and especially it is not free from indigo-red; in this case the solution cannot be used for accurate determinations. If 20 c.c. of the indigo solution requires about the same quantity of permanganate solution, the former is of the proper concentration, but if much more or less is necessary then the indigo solution must be correspondingly diluted, or strengthened by adding more indigo-carmine, and its relation to the permanganate solution again determined. The solution which has been rendered yellow is kept for comparison.

4. Twenty c.c. of the indigo solution and 10 c.c. of the tannin extract are mixed with 1 litre of water, and permanganate solution is run in, in the space of about four minutes, until the liquid exhibits the same pure yellow colour as that obtained by standardising the permanganate with indigo solution in 3. If considerably more than 30 c.c. of the permanganate is needed, the amount of tannin extract employed was too large. The test is then repeated with a correspondingly smaller number of c.c., and the quantity of permanganate solution corresponding with the amount of tannic acid together with "other substances," is ascertained by deducting from the total the quantity of permanganate solution required for the indigo.

5. Five grams of extracted bone or horn cartilage is moistened with exactly 50 c.c. of water in a flask, 50 c.c. of the liquid containing the tannin matter is then added, the flask is corked, allowed to remain for 24 hours with frequent shaking, and a little of the liquid is filtered off and tested to see whether all the tannic acid has been thrown down. This is effected by concentrating the filtered sample by evaporation, and adding a clear solution of gelatin saturated with salt; if a precipitate is produced, more of the extracted bone or horn cartilage is added to the contents of the flask, and the digestion continued until the object is attained. If all the tannic acid is precipitated, the liquid is filtered, 40 c.c., corresponding with 20 c.c. of the liquid containing tannic acid,

is measured off; 20 c.c. of the indigo solution, and 1 litre of water are added, and then the permanganate solution as above, until the liquid has become pure yellow. In this way, the amount of permanganate required by the "other substances" in 20 c.c., and by halving, the quantity for 10 c.c., of the extract, is ascertained, and by difference the quantity of permanganate of potassa corresponding with the tannin.

One example will serve as explanation.

Ten grams of chestnut wood yielded 1000 c.c. of extract.

One hundred c.c. of permanganate solution corresponded with 0·1819 of crystallised oxalic acid.

Twenty c.c. of indigo solution required 21 c.c. of permanganate solution. Twenty c.c. of indigo solution + 10 c.c. of chestnut-wood extract required 32 c.c. of permanganate solution. On deducting from this the 21 c.c. corresponding with the indigo solution, there remained for the tannic acid and "other substances" 11 c.c.

Five grams of extracted bone + 50 c.c. water + 50 c.c. of chestnut-wood extract yielded a filtrate free from tannin, of which 40 c.c. (= 20 c.c. of extract) + 20 c.c. of indigo solution, required 22·6 c.c. of permanganate, the amount, therefore, referable to the "other substances" in 20 c.c. of extract is 22·6 − 21 = 1·6 c.c., that in 10 c.c. being = 0·8 c.c.

If now this 0.8 c.c. is deducted from the 11 c.c. obtained above, 10·2 c.c. of permanganate solution is left for the tannic acid in 10 c.c. of the extract.

III. CALCULATION.

From NEUBAUER'S experiments, it has been ascertained that 63 grams of crystallised oxalic acid (as also 56 parts of iron in the state of ferrous oxide) and 41·57 grams of tannic acid decompose equal quantities of permanganate solution, being equivalent in this respect.*

If the substances contained the same tanning matter as gall nuts, that is tannic acid, the amount of tanning matter could easily be calculated and expressed per cent. from the figures obtained in II., that is from the quantity of permanganate solution necessary to oxidise the tanning matter. As, however, the various tanning materials do not, as a rule, contain tannic acid but rather other tanning matters which are practically unknown in a pure state and whose decomposing effect on permanganate of potassa is also unknown, it is therefore solely by a sort of compact that notwithstanding this, the amount of tanning matter in certain tanning materials is calculated by the above-mentioned ratio from the amount of permanganate of potassa required. For example, according to this practice, 12·24 per cent. of tanning matter is found in the chestnut wood serving as example in II., and in the following manner: 100 c.c. of permanganate solution corresponding with 0·1819 gram of oxalic acid, or, taking the proportion 63 : 41·57 with 0·120 gram of tannin; 1 c.c., therefore, corresponds with 0·0012 gram of tannic acid. For the oxidation of the tannin in 10 c.c. of chestnut-wood extract 10·2 c.c. of permanganate solution were required, which, therefore, equals 10·2 × 0·0012 grams = 0·01224 gram of tannic acid. If, however, 10 c.c. of the chestnut-wood extract contain 0·01224 gram of tannin, 1000 c.c. will contain 1·224 grams, and as this is derived from 10 grams of chestnut wood, 100 grams of the latter will contain 12·24 grams of tanning matter.

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* It may here be mentioned that ULBRICHT (Annalen. der Oenologie, 3, 63) and also OSER (Sitzungsber. der mathem.-naturwisssenschaftl. Classe der R. Akademie in Wien, 72, 186) confirm the proportion here given; on the other hand, COUNCLER and SCHRÖDER (Ber. deutsch. chem. Gesell., 15, 1373; Zeitschr. f. anal. Chem. 22, 274) have called it in question; they found the relation to be 63 : 34·25.

It should be noted that this and other analogous calculations have no scientific basis, and the result founded thereon as expressing the percentage of tanning matter means, in fact, merely that the tanning matter in 100 grams of this particular chestnut wood reduces the same amount of permanganate solution as 12·24 grams of tannic acid, presupposing the calculation to be based on the proportion of 63 oxalic acid to 41·57 tannic acid.

Even as NEUBAUER and others for tannic acid, so OSER[*] for quercitannic acid has sought to determine in what proportion this is equivalent to oxalic acid with respect to permanganate solution. He found that 63 of crystallised oxalic acid and 62·32 of oak tannin decolorised equal quantities of permanganate of potassa, but does not himself consider the last figure as in any way trustworthy. SIEMAND, from preliminary experiments, found the proportion 63 : 60·11.

No comparative figures are required to show what differences must arise in estimating the tanning matter in a tanning material; such as for example chestnut wood, if on the one hand, NEUBAUER'S ratio 63 : 41·57, or on the other COUNCLER and SCHRÖDER'S of 63 : 34·25; or again that arrived at for quercitannic acid, namely 63 : 62·32 or 63 : 60·11, is taken as the basis of calculation, and it is therefore always essential not only to state the result but also the proportions between oxalic acid and tannic acid used for the calculation.

B. K. HAMMER'S Method.[†]

§ 280.

This process worked out in the author's laboratory in 1860 gives, with respect to solutions of tannin, by careful working, thoroughly trustworthy and accurate results, is simple in performance and suitable both for scientific and technical purposes; compare also FR. GAUHE,[‡] W. HALLWACHS,[§] TH. SALZER,[||] FR. KATHREINER,[¶] PROCTER, and HEWITT.[**] NEUBAUER[††] made use of this method for estimating the tannin in the solution with the help of which he ascertained the equivalent relation between oxalic acid and tannic acid with respect to permanganate solution.

In the case of other tanning principles, the objection may be raised that it is not known whether the relation between content and specific gravity of their solutions corresponds with the values determined for tannic acid solution; this objection which in all probability is not a weighty one, can, however, only be completely removed by experimental determinations of this relationship for solutions of other tanning principles.

In the case of solutions of tanning material which contains pectinous substances, HAMMER's original process must, as J. LÖWE* found, be modified in order to obtain correct results, as will be shown hereafter.

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[*] Sitzungsber. der mathematisch-naturwissenschaftl. Classe der K. Akademie in Wien, 72, 186.

[†] Journ. f. prakt. Chem. 81, 159.

[‡] Zeitschr. f. anal. Chem. 3, 128.

[§] *Ibid.* 5, 231.

[||] *Ibid.* 7, 70.

[¶] *Ibid.* 18, 113.

[**] *Ibid.* 18, 115.

[††] *Ibid.* 10, 2.

a. Principle.—If the specific gravity of a liquid containing tannin along with other substances in solution is determined, and if the tannin alone is then removed—the liquid not being thereby diluted or otherwise altered—and if finally the specific gravity is re-determined, the decrease in specific gravity will be proportional to the percentage of tannin originally present in the solution. It is only necessary therefore to have an exact table, showing the relation between the specific gravity of tannin solutions of different degrees of concentration, in order to be able to estimate the amount of tannin in the solution from the difference.

b. Requisites.—To determine the specific gravity either a pyknometer (this vol. p. 483), or a fine hydrometer is required; the latter instrument should give either specific gravities from 0 to 1·0201 or the percentages of tannin corresponding with these specific gravities for solutions of pure tannin in water.

To remove the tannin from its solutions, HAMMER uses finely divided or powdered hide. A piece of hide prepared for tanning is thoroughly washed with water, stretched on a board, dried at a gentle heat, and converted into a coarse powder by means of a rough file, the powder being preserved for use in a well-closed bottle. Instead of hide, and indeed with better results, the preparations mentioned on p. 485 of this vol. can be used, namely, the gelatin-forming tissue of bones, or horn cartilage, because these give up less soluble substance to water than hide does (see this vol. p. 485). 4 parts of hide powder, bone preparation, or horn cartilage, are sufficient to remove 1 part of tannin from a liquid. When using it, a weighed quantity of the preparation is soaked in water, and then well squeezed, so that the adherent water may not dilute the solution with which the material is to be brought in contact. If it is thought desirable to entirely avoid this small source of error, the pressed material can be again weighed, and the amount of water which it has absorbed subsequently taken into account when the calculation is made.†

The relation between specific gravity and percentage for dilute tannin solutions is given in the table on the next page, which must also be used for solutions of other tanning materials until corresponding tables are specially prepared.

c. The Process.—In the first place, the tannin to be estimated must be obtained in a clear and not too dilute solution. Barks and similar materials are first boiled, in a finely divided condition, with water, and then completely exhausted in a displacement apparatus; inspissated vegetable juices are rubbed up with water in a mortar, strained through linen, and the residue well washed. As a rule, 1 part of substance yields 10 parts of solution. If the solution obtained on complete exhaustion is too dilute, it must be concentrated by evaporation. From 200 to 500 c.c. of a solution of the proper concentration will be required. If the extract contains pectinous substances these must be removed, using for this purpose, J. Lowe's method as described in this vol. p. 486.

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* Zeitschr. f. anal. Chem., 4, 368.

† TH. SALZER (Zeitschr. f. anal. Chem. 7, 71) obtained results which did not vary appreciably on treating the same solution of tanning matter at one time with the hide powder dried at 100°, and at another with the same powder moistened and gently squeezed. In this way, using hide powder dried at 100°, and carefully washing it after it had taken up the tanning matter, collecting on a double filter, drying at 100°, and re-weighing, he obtained from the increase in weight a (sufficiently concordant) means of controlling the value obtained by taking the specific gravity.

Sp. gr. at 15°.	Percentage of tannin.	Sp. gr. at 15°.	Percentage of tannin.	Sp. gr. at 15°.	Percentage of tannin.
1·0000	0·0	1·0068	1·7	1·0136	3·4
1·0004	0·1	1·0072	1·8	1·0140	3·5
1·0008	0·2	1·0076	1·9	1·0144	3·6
1·0012	0·3	1·0080	2·0	1·0148	3·7
1·0016	0·4	1·0084	2·1	1·0152	3·8
1·0020	0·5	1·0088	2·2	1·0156	3·9
1·0024	0·6	1·0092	2·3	1·0160	4·0
1·0028	0·7	1·0096	2·4	1·0164	4·1
1·0032	0·8	1·0100	2·5	1·0168	4·2
1·0036	0·9	1·0104	2·6	1·0172	4·3
1·0040	1·0	1·0108	2·7	1·0176	4·4
1·0044	1·1	1·0112	2·8	1·0180	4·5
1·0048	1·2	1·0116	2·9	1·0184	4·6
1·0052	1·3	1·0120	3·0	1·0188	4·7
1·0056	1·4	1·0124	3·1	1·0192	4·8
1·0060	1·5	1·0128	3·2	1·0196	4·9
1·0064	1·6	1·0132	3·3	1·0201	5·0

The prepared tannin solution is now weighed, and for simplicity in reckoning, it is convenient to make up the weight of the liquid to a round number of grams by the addition of water, mixing the solution uniformly, and determining the specific gravity by a pyknometer or hydrometer. If the latter is used, care must be taken that the cylinder is dry, or rinsed with a portion of the liquid to be tested; that no air-bubbles adhere to the float; and that while reading, the eye is placed on a level with the lower border of the meniscus of the liquid.

Somewhat more of the tannin solution than is required for determining the specific gravity is now weighed off in a flask, which must be dry, or rinsed with the liquid containing the tannin; four times the quantity of powdered hide, bone preparation, or horn cartilage required for the amount of the tannin present (as calculated from the sp. gr.) is added, the flask is corked, shaken briskly for some time, and allowed to remain for 24 hours, shaking it at intervals. The precipitating material and the liquid to be precipitated need only be weighed approximately. The solution, now free from tannin, is filtered through linen directly into the cylinder of the hydrometer or into the pyknometer, and the specific gravity re-determined.

The hydrometer may be graduated specially as a tannin meter: in that case, the difference between the two readings represents at once the percentage of tannin in the examined fluid. If, on the contrary, the instrument used gives merely the specific gravity, or if the latter has been determined by a pyknometer, 1 is added to the difference between the specific gravities, and the number in the table gives the corresponding percentage of tannin in the liquid. This being known, a simple calculation will give us the absolute weight of tannin in the whole quantity of the solution, or in other words, in the quantity of substance taken.

d. Example.—From 40 grams of oak bark, 500 grams of solution of sp. gr. 1·0068 at 15° are obtained, corresponding with an apparent content of tannin of 1·7 per cent. 200 grams of the liquid are now weighed off; this contains apparently 3·4 grams of tannin; 4 times the quantity, or 13·6 grams of hide filings is added, after they have been macerated and squeezed. The sp. gr. of the filtered solution as determined by the hydrometer, is 1·0032, corresponding with an apparent content of tannin of 0·8. The difference of the two estimations, 1·7 and 0·8, is precisely 0·9; thus the solution contained 0·9 per cent. of tanning matter. If however 100 grams contained 0·9 gram, then the 500 grams would contain 4·5 grams, and as these were derived from 40 grams of oak bark, the percentage content would be 11·25 grams; of course, identical results would be obtained, if the difference of specific gravity were taken as the basis of calculation. This was 1·0068—1·0032 or 0·0036. By adding 1 to this, 1·0036 is obtained, corresponding—see the table—with 0·9 per cent.

C. Gravimetric modification of Hammer's method.

§ 281.

As may easily be seen, tannic acid may be also gravimetrically estimated by using HAMMER's principle. This modification was first proposed by A. MUNTZ and RAMSPACHER,* and recently by SIMAND.† The latter employed it as a means of checking the relation which tannin and quercitannic acid, and oxalic acid or iron dissolved as ferrous salts, bore respectively to permanganate of potassa.

To carry it out, extracts must be prepared as in HAMMER's method, and must be, as in the latter, free from pectinous substances.

A suitable quantity (SIMAND employed 100 c.c.) must be evaporated in a tared platinum basin, the residue dried at 100° until the weight is constant, weighed, incinerated, and the mineral constituents deducted from the residue, so as to give the total amount of dissolved organic matter.

Further, an equal quantity of the extract containing the tanning principle is mixed with the necessary amount of horn cartilage and allowed to act during 24 hours in order to precipitate all the tannic acid. At the end of this time it is filtered, washed thoroughly, and the filtrate evaporated as above; it is then dried at 100°, incinerated, and the mineral constituents deducted from the total weight of the residue. This gives the amount of substance which is not removed by the horn cartilage (*i.e.* that which is not tanning principle). Finally by deducting this from the sum of the tanning principle and other substances first obtained, the difference gives the weight of tanning principle.

D. Other methods for estimating the tanning principle.

As it is not the object of this work to give in detail the numerous other methods proposed and employed formerly or in recent times for

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* Compt. rend. 79, 380; Zeitschr. f. anal. Chem. 13, 462.

† Dingl. polyt. Journ. 246, 41; Zeitschr. f. anal. Chem. 22, 598.

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the estimation of tanning principles, reference must be made to the "Zeitschrift für analytische Chemie," 1. 103, 104,—2. 137, 287, 419,—3. 484,—5. 1, 455, 456,—10. 1,—13. 243,—14. 204,—15. 112,—16. 123,—18. 112,—21. 414, 552.

The following have published critical, or partly critical, investigations on the methods of estimating tanning principles; FR. GAUHE (Zeitsch. f. anal. Chem. 3, 122; HALLWACHS (*Ibid.* 5, 231); TH. SALZER (*Ibid.* 7, 70); C. O. CECH (*Ibid.* 7, 130); PH. BÜCHNER (*Ibid.* 7, 139); NEUBAUER (*Ibid.* 10, 1); GÜNTHER (*Ibid.* 10, 354); KATHREINER (*Ibid.* 18, 113), and others.

IV. ESTIMATION OF ANTHRACENE.

§ 282.

Since the production of alizarin from anthracene has been carried out on a large scale, the estimation of the amount of anthracene in crude anthracene has become a problem of frequent occurrence in chemical laboratories. The process which was thoroughly worked out in the laboratory of MEISTER, LUCIUS and BRÜNING by E. LUCK, and first published in 1873,* and based on the conversion of anthracene into anthraquinone, has been developed into that made public by MEISTER, LUCIUS and BRÜNING in October 1876,† and now universally employed. It will be convenient to give an account of this method here, supplementing it with those modifications adopted in the author's laboratory which have proved to be of value.

1. It is of the utmost importance to procure a homogeneous sample and to take care that in its preparation it is not altered by the evaporation of adhering volatile hydrocarbons. With this object, the crude anthracene is emptied into a basin and *quickly* mixed with a spatula or piece of card, after crushing any large lumps, and transferred to a stoppered glass vessel. The sample for analysis is weighed in closed tubes which are re-weighed after the anthracene has been emptied out. For each analysis, about 1 gram (0·97—1·03 gram is required).

2. The weighed anthracene is placed in a 500 c.c. flask, and 45 c.c. of glacial acetic acid is poured on it. The stopper of the flask is pierced with two holes, one of them furnished with a funnel tube fitted with a glass tap and terminating below in a narrow opening, whilst the other is provided with a glass tube bent at an obtuse angle and connected with a reflux condenser. The contents of the flask are now heated to boiling, and kept boiling, while a solution of 15 grams of chromic acid ‡ in 10 c.c. of glacial acetic acid and 10 c.c. of water is allowed to drop in from the funnel tube so slowly that the operation lasts for two hours; when all the chromic acid has been added, the contents of the flask are kept boiling for another two hours.

3. The flask is left for 12 hours, 400 c.c. of cold water is added, and the whole left for another 3 hours. The precipitated anthraquinone is then collected on a filter, and washed, first with cold water until the filtrate is no longer acid, then with about 200 c.c. of a boiling potash

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* Zeitschr. f. anal. Chem. 12, 347, and 13, 251.

† *Ibid.* 16, 61.

‡ This must be prepared according to FRITZSCHE's method, using *pure* sulphuric acid.

solution containing 1 per cent. of caustic potash, and finally with pure hot water until the washings no longer give an alkaline reaction.

4. The anthraquinone is now rinsed by means of a fine but strong stream of water into a platinum basin of approximately known weight, the filter being spread out on a glass plate so as to completely remove the anthraquinone; the whole is then dried at 100°, the still impure anthraquinone is weighed approximately, ten times its weight of fuming sulphuric acid of 68° B = 1·86 sp. gr. is poured on to it, and the mixture heated for 10 minutes in a water-oven (Vol. I. p. 44, fig. 31), the water being kept briskly boiling.

5. The anthraquinone solution thus obtained is poured into a shallow porcelain dish, and this, together with the platinum dish, still containing small portions of the solution, is left in a damp place for 12 hours so as to allow of the absorption of water. At the expiration of this time, the platinum dish is washed out into the porcelain basin, using 200 c.c. of cold water; the anthraquinone is now collected on a filter and washed first with cold water until the washings are no longer acid, then with about 200 c.c. of boiling dilute potash solution (containing 1 per cent. of hydrate of potassa), and finally with hot water until the washings no longer have an alkaline reaction.

6. The washed anthraquinone is rinsed into a platinum dish, the whole evaporated on the water-bath, and the residue dried at 100° until the weight is constant. The platinum dish is then carefully heated so as to completely volatilise the anthraquinone but without setting it on fire, and the dish containing a little ash and carbonaceous matter is again weighed. The difference between the weighings gives the weight of the anthraquinone, and this multiplied by 0·856 gives the anthracene.

III. ESTIMATION OF THE INORGANIC MATTER OF PLANTS.*

§ 283.

Since researches in agricultural chemistry have fully established the fact, that each plant requires certain inorganic constituents for its development, a strong desire has arisen to ascertain what inorganic constituents are necessary for the several plants, and more especially for cultivated plants, and also for weeds, as the latter give us an insight into the constituents of the soil. At first, endeavours were made to obtain this knowledge by analysis of the ash remaining when either the entire plants or particular parts of them, the seeds for instance, were incinerated. Since it is now admitted, however, that this object cannot be fully attained in this way, as during the incineration of a plant, some of the inorganic constituents must be lost, whilst others may be lost, the ash analysis has to be supplemented by special estimation of the individual elements, as the methods hitherto employed for attaining this object in other ways, have not been satisfactory.*

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* As the estimation of the inorganic constituents of animal substances is less frequently undertaken than their determination in plants, since they are usually required for scientific rather than for technical purposes, a detailed description has been omitted in the text; it may here be noticed, however, that, in general, the same processes may be used as those which are given in the text. Substances which fuse are first heated, according to H. Rose, in a platinum dish, stirring meanwhile, until they cease to be liquid and the greater part of the organic matter is destroyed. The nearly carbonized residue is then transferred to a platinum or clay crucible furnished with a close-fitting lid, and heated to dull redness. The charcoal thus obtained is burnt with the aid of spongy platinum. Strecker's method of incineration, with addition of baryta, is also well adapted for animal substances. According to Slater (Chem. Gaz. 1855, 53), a particularly effective way of incinerating animal substances, is to mix them with pure, dry, finely pulverized peroxide of barium, and then ignite the mixture. In his paper on the subject (Ann. d. Chem. u. Pharm. 73, 370), Strecker calls attention to the fact that the ashes of animal substances often contain no inconsiderable quantity of cyanates. These salts are most easily destroyed by moistening the ash with water, and then heating gradually to redness; a single moistening usually sufficing to convert the cyanates into carbonates. For the estimation of chlorine, animal matter should be

In the following section, the *Ash Analysis* is described under A; the *Supplementary Estimations* under B; and the *Arrangement of the Results* under C.

A. Ash Analysis.

As the ashes of plants, according to the researches hitherto made, contain but a limited number of acids and bases, certain methods generally applicable to their analysis have been devised, and as these offer many peculiarities, and are frequently employed, those which appear to be the simplest and best will be described here, a critical discussion of the very numerous and essentially different methods proposed not being within the scope of the present work.

The following are the substances generally found in larger quantities in the ashes of plants:

Bases.

Potassa, soda, lime, magnesia, ferric oxide, protosesquioxide of manganese.

Acids, or similar substances.

Silicic acid, phosphoric acid, sulphuric acid, carbonic acid, chlorine.

Besides these, lithia, rubidia, strontia, baryta, oxide of copper, and

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incinerated after adding carbonate of soda (1·5–2·5 grams to 50 grams of the organic substance) (Behaghel von Adlerskron, Zeitschr. f. anal. Chem. 12, 405). Lastly it should be noted that if in estimating the phosphorus and sulphur, it is desired to ascertain the total amount, the methods suited for the estimation of phosphorus and sulphur in organic substances and described in §§ 188 and 189 must be adopted. Special details as to the method of analysis of the ash of animal substances, are also given in F. Verdeil's paper on the analysis of the ash of the blood of man and several animals (Ann. d. Chem. u. Pharm. 69, 89; Pharm. Centralbl. 1849, 198; Liebig and Kopp's Jahresber. 1849, 598); and Fr. Keller's paper on the ash of flesh and broth (Anal. d. Chem. u. Pharm. 70, 91; Pharm. Centralbl. 1849, 581; Liebig and Kopp's Jahresber. 1849, 599).

* Caillat states that, by treating herbaceous plants (clover, lucern, sanfoin) with dilute nitric acid, the inorganic constituents may be so completely removed that the readily combustible residuary mass from 10 grams of vegetable matter, on incineration, left only 18 to 22 milligrams of ash, consisting of silicic acid and ferric oxide. He states, moreover, that this method of treating the plant gives a larger quantity of inorganic constituents, more particularly of sulphuric acid, than is obtained by the incineration of the plant (Compt. rend. xxix. 137; Liebig and Kopp's Jahresber. 1849, 601).—Rivot, Beudant and Daguin (Compt. rend. 1853, 835; Journ. f. prakt. Chem. 61, 135) propose destroying the organic matters by treating them with solution of potassa and passing chlorine into the mixture. The experiments of W. Knop may also be alluded to here; he endeavoured to determine the mineral substances required for the nourishment of plants, by allowing the plants to vegetate in solutions containing known quantities of inorganic compounds, subsequently estimating the amount left in solution.

fluorine, are frequently found, occasionally alumina (for example, in the ashes of the *Lycopodiaceæ*, in comparatively large proportion), iodine, bromine, cyanides and cyanates (only in the ashes of substances abounding in nitrogen), boric acid, sulphides, and also traces of oxide of zinc, or of other oxides of the heavy metals. Most of the substances here named are unquestionably original constituents of the plants; many on the other hand may have been present as such in the vegetable, or they may have been formed in the process of incineration; lastly, some of them certainly owe their origin to that destructive process. Thus the sulphates and, as an exception, even the carbonates, found in the ash, may have been original constituents of the plant; but they may also have been formed in the process of incineration, by the destruction of salts of organic acids, and by the combustion of the sulphur which every plant contains in the unoxidized state; thus the metallic sulphides are formed by the action of the charcoal on sulphates if there is an insufficient supply of air, the cyanides of the metals are due to the effect of heat on nitrogenous charcoal in contact with alkali carbonates, and the cyanates to the oxidation of the metallic cyanides, &c.

From the varieties of these constituents, and the circumstance that some of them are usually present in very small quantities only, it is by no means an easy task to devise methods which are universally applicable; more especially, as it is always a desideratum to unite accuracy with despatch.

In the first place, the *preparation of the ash for the purpose of analysis* will be considered, and then *the analysis itself.*

I. Preparation of the Ash.

§ 284.

In preparing an ash, the following conditions must be fulfilled.

1. The plant or part of a plant to be incinerated must be dried, divided into suitable pieces, and freed from all adhering impurities.
2. The ash must be as free as possible from unburnt matters.
3. As far as possible, loss of the essential constituents must be avoided in the process of incineration.

To satisfy the *first* condition, the plants or parts of plants intended for incineration must be carefully selected and cleaned, and, if necessary, cut up and dried. It is not always practicable to rub or brush away sand or clay, more especially from small seeds. H. Rose gives the following directions for cleaning the latter. The seeds are treated in a beaker, with a moderate quantity of distilled water, well stirred a few moments with a glass rod, and then placed on a sieve sufficiently coarse to allow the fine sand to pass through whilst retaining the seeds. This operation is repeated several times, but care must be taken never to leave the seeds long in contact with water, otherwise soluble salts may be extracted from them. Finally, the seeds are placed on a linen cloth, and rubbed between its folds, so as to remove the fine sand still adhering to them; seeds cleaned in this manner are almost entirely free from foreign matters. They are then dried ready for incineration. The jumping about of the seeds when heated may be obviated by previously crushing them.

In cutting up plants, a perfectly clean knife or pair of scissors must be used, and in drying, care must be taken to protect them from dust, and to avoid any loss of the sap.

For the fulfilment of the *second* and *third* conditions, the principal point to be attended to is that the incineration must be effected at the lowest possible temperature (a dull red heat), and with an adequate, but not too plentiful, supply of air. If the draught is too strong, it is apt to carry away particles of the ash, whilst, if too feeble, the operation lasts too long, and the process of reduction takes place more easily. If ignited too strongly, not only will the metallic chlorides and carbonates and the phosphates of the alkalies fuse and envelop the carbon, thereby very greatly impeding its combustion, but the excessive heat will cause volatilisation of both the alkali chlorides and carbonates;[*] even phosphoric acid may be lost in this way, for as ERDMANN first showed, the acid phosphates of the alkalies, when ignited with carbon, are converted into neutral salts, with reduction and volatilization of part of the phosphorus. A loss of chlorine cannot be avoided by care in incineration, since the acid products formed in the dry distillation of organic substances, expel hydrochloric acid, as H. ROSE,[†] R. WEBER,[‡] and BEHAGHEL VON ADLERSKRON,[§] have shown. Although loss of chlorine or phosphoric acid may be effectually guarded against by employing proper methods of incineration, and, if need be, by mixing carbonate of soda, baryta, or lime with the substance intended for incineration, this is not the case with carbonic acid. The estimation of the carbonic acid in the ash will, therefore, never enable us to draw any trustworthy inference as to the constituents of the incinerated vegetable, for it is incorrect to suppose that the presence of carbonates in the ash of a plant, itself containing no carbonates, may be regarded as a proof of the presence of salts of organic acids in that plant, since alkali carbonates may easily be formed by the action of nitrates on charcoal, or by the action on alkali chlorides of the acid products formed by the destructive distillation of organic substances, and subsequent decomposition of the alkali compounds thus produced; moreover, as STRECKER has shown, alkali carbonates are formed, and also alkali pyrophosphates, when alkali orthophosphates are ignited with a large excess of sugar, or with the charcoal from the latter. When these facts are considered, and further that the reverse action can take place, namely, that alkali pyrophosphates when strongly ignited along with alkali carbonates are converted into orthophosphates, it can easily be understood that the detection of orthophosphates or pyrophosphates in an ash may also depend on the manner in which the latter has been obtained.

But least of all will the estimation of the sulphuric acid in the ash of a plant enable us to judge of the constituents present, even if the incineration is effected with the addition of an alkaline earth, for plants contain, in the first place, sulphuric acid in the form of sulphates, and secondly, sulphur in organic combination, especially in the proteid substances. If the incineration is properly carried out, the whole of the sulphates present will indeed be obtained, but certainly, in many cases, these will be increased by other sulphates formed during the operation. This, however, is certain, that the quantity of sulphuric acid found in the ash of a plant can never serve to determine, even approximately, the amount of sulphur contained in the plant.*

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[*] See LANDOLT, Zeitschr. f. anal. Chem. 7, 20, ed. A. VOGEL, *ibid.* 7, 149.

[†] Pogg. Annal. 80, 113.

[‡] *Ibid.* 81, 407.

[§] Zeitschr. f. anal. Chem. 12, 405.

The several methods of incineration will now be described.

1. Incineration in a Muffle or in a Crucible.

Incineration in a muffle, which was first recommended by ERDMANN,† and afterwards by STRECKER,‡ has almost entirely superseded the old way of burning the substances in Hessian crucibles placed in an inclined position.

The muffles employed by the author are made of the same material as Hessian crucibles, and are in internal measurement 25 cm. deep, 17 cm. broad, and 12 cm. high. They are placed in furnaces, have no draught-pipe, and the mouth is loosely closed with a perforated door. The circulation of air thus created is quite sufficient for the combustion of the charred substance.

a. The substance which it is intended to incinerate (about 100 grams) is dried at 100 or 110°, succulent roots and fleshy fruits being cut up and laid on glass plates. The dried substance is weighed, and after being put into a shallow platinum or porcelain capsule, or, still better, into a shallow platinum or porcelain dish fitting exactly into the muffle, is introduced into the latter, which is then gradually heated. As soon as the evolution of combustible products ceases, the heat is increased a little, but not beyond a very faint red heat not visible in daylight. At this temperature, which is not sufficiently high to fuse either chloride of sodium or pyrophosphate of soda, the carbon burns with feeble incandescence, and 12 hours suffice to obtain a quantity of ash sufficient for the purposes of analysis, and free from carbon. Substances to which this mode of incineration is unsuited, are first charred in a large covered platinum or Hessian crucible, at a gentle red heat, and the charred mass is subsequently incinerated in the muffle. As a general rule, it is not advisable to stir the substance undergoing incineration, since this would tend to diminish its porosity. According to STRECKER, no chloride of sodium volatilizes in this process of incineration.

After completing the combustion, any alkalies or alkaline earths which may have been produced from their carbonates by loss of carbonic acid are, as far as possible, reconverted into anhydrous neutral carbonates; the ash is then weighed, ground up, mixed, and placed in a tightly closed glass bottle.

The conversion of the alkalies or alkaline earths into carbonates can be effected, (α) by placing the moistened ash under a tubulated bell jar, passing in carbonic acid through the neck, allowing it to remain for a considerable time, and repeating the operation, if necessary, after stirring up the ash; (β) by repeatedly evaporating the ash in the water-bath along with carbonic acid water or a solution of carbonate of ammonia; finally, the residue is dried and heated moderately until all the water is driven off. In this way the alkalies and lime (in the case of an ash prepared with hydrate of baryta, see below, 4, p. 500, and also baryta) are converted into neutral carbonates, but not magnesia, which, if existing as such in the ash, will also be obtained as such, or at all events partly so, in the ash treated with carbonic acid.

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* Comp. Mayer, Ann. d. Chem. u. Pharm. 101, pp. 136 and 154.

† Ann. d. Chem. u. Pharm. 54, 353.

‡ *Ibid.* 73, 366.

b. If incineration has to be carried out on a small scale, a small inclined platinum crucible heated with gas or a spirit lamp is used. This crucible should be fitted with a slightly arched disk of burnt clay, or a sheet of asbestos cardboard, and fitting as tightly as possible, at $\frac{3}{4}$ths of the height, into the circular opening. The inclined position is given to the apparatus by the use of a tripod with one short leg. If the crucible is then heated from below, the entrance of air is not interfered with by the burning gases, and the incineration is completed exactly as in a muffle (J. Löwe,* G. Lunge†). As regards the further treatment of the ash, compare *a*.

c. In the case of vegetable substances the ash of which abounds in alkali salts, especially chlorides, and consequently is readily fusible, it is generally advisable to char them in a crucible, at the lowest possible temperature, by long-continued heating, then to treat them with water until the soluble salts are extracted, dry the residue, and incinerate it in a platinum dish or platinum crucible. After the ash of the insoluble portion has been treated with carbonic acid water or carbonate of ammonia, it is weighed (see *a* above), the solution is diluted to the exact point to give just as many tenth, half, or whole cubic centimetres of liquid as there are milligrams of ash of the insoluble portion, and later, in the analysis, the weighed quantities of the ash are severally mixed with a corresponding number of cubic centimetres of the solution. The author has frequently employed this method with great success.‡ In order to ascertain the total amount of ash, a measured portion of the solution is evaporated to dryness with the addition of carbonic acid water or carbonate of ammonia, heated moderately, and the dry residue weighed. This part is then calculated with reference to the whole, and the result (representing the residue which the entire solution would leave on evaporation) added to the weight of the ash of the insoluble portion.

2. Incineration in a Dish, with the aid of an Artificial Current of Air (F. Schulze§).

a. The organic substance, dried at 100°, and weighed, is charred in a crucible, at a gentle red heat, and the charred mass is transferred to a shallow platinum dish; a triangle of platinum wire is laid on the dish, and on the triangle is placed an ordinary lamp chimney or Argand lamp glass (or a sufficiently wide neck of a retort), the chimney being supported by means of a retort holder so as to hold it firmly over the dish, which is heated by a small gas lamp or a spirit lamp. The increased current of air caused by the chimney, which may be regulated by taking a longer or shorter one, and placing it higher or lower, suffices to effect the complete incineration, even of cereal grains, at a surprisingly low temperature.|| When the incineration is completed, the ash is weighed and treated as in 1.

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* "Taschenbuch für die Soda-&c. Fabrication," p. 83 (Berlin: F. Springer. 1883).

† Zeitschr. f. anal. Chem. 20, 223.

‡ Journ. f. prakt. Chem. 70, 85.

§ Communicated to the author by letter.

|| F. Schulze employs this method also for the incineration of filters; he places the crucible with the filter in the dish.

b. In incinerating vegetable substances rich in alkali salts, the method described in 1 *c* is recommended.

3. Incineration with the aid of an Artificial Current of Air (Hlasiwetz*).

This method requires a silver, platinum, or porcelain tube of the form of a tobacco pipe. For difficultly combustible charcoal, it should be cylindrical, 21 cm. long, 4·5 cm. wide, and with the lower end tapering to a point. A platinum plate with 6—8 small perforations prevents charcoal or ashes falling out. For readily combustible charcoal, a conical or crucible-like shape is given to the tube. This pipe is fitted air-tight into one tubulure of a two-necked Woulff's bottle, which is connected in the usual way with a second and third, and the latter with a very large aspirator (a barrel) or a water pump. If water is allowed to flow from the barrel by opening the cock, or if suction is applied by means of the pump, air rushes in through the pipe, and passes through the water in the second and third bottles which are not quite half filled with it. The process is conducted as follows. The suitably comminuted organic substance is charred in a porcelain crucible with the lid on; and as soon as the gases cease to burn, the feebly glowing charcoal is introduced into the pipe through a funnel, and the water is allowed to run out of the aspirator in a gentle stream, or moderate suction is applied by means of the water pump, the aspiration being so regulated as to insure proper combustion at a moderate temperature. From time to time, the mass is piled together in a heap by means of a platinum wire; finally the ash is heated for a short time in a platinum dish, to insure the combustion of the last remaining particles of charcoal. In the water of the Woulff's bottles, traces of fixed salts are found, more particularly of metallic chlorides; also carbonic acid and ammonia. If the salts are weighable, they must be determined.

4. Incineration in a Muffle, with the addition of Baryta (Strecker†).

The organic substance is dried at 100°, and charred slightly, in a porcelain or platinum dish, over the lamp. The charred mass is moistened with a concentrated solution of *pure* hydrate of baryta in such quantity that the ash left on incineration may contain about half its weight of baryta. The moistened mass is dried again, and then burnt in the muffle at the lowest possible temperature; the ash, kept from fusion by the baryta, remains bulky and loose, thus allowing complete combustion of the carbon to take place. The residue should still contain a considerable excess of carbonate of baryta. If this is not the case, there is reason to apprehend, at all events in some incinerations, a loss of phosphorus, so that it is advisable in such cases to incinerate a fresh portion, using a larger quantity of baryta water. The residue is then reduced to a fine powder, and intimately mixed.

As E. von Raumer,‡ on incinerating maize according to the method just described, observed that the ash contained pyrophosphates, and he advised, in order to avoid this happening in the incineration of grain, that it should be soaked in baryta water and then dried and incinerated. The ash of maize treated in this way contained orthophosphates only.

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* Ann. d. Chem. u. Pharm. 97, 244.

† *Ibid.* 73, 366.

‡ Zeitschr. f. anal. Chem. 20, 375.

If the amount of ash is to be determined from that containing baryta, a measured quantity of baryta water containing a known amount of baryta must be added, and the ash treated as in 1 *a*, so as to convert into carbonates, the alkalies and alkaline earths whose carbonic acid has been driven off. Finally, it must also be noted that the ash containing baryta, as a rule, that is, when a very large excess of baryta has not been added, no longer contains all the chlorine originally present in the substance incinerated. The ash constituents will therefore come out too low, and a separate portion should be used for the accurate estimation of the chlorine in the organic substance (see this vol. p. 510, BUNGE,* BEHAGHEL VON ADLERSKRON†).

5. Incineration with the aid of Spongy Platinum (H. ROSE).

About 100 grams of the substance dried at 100°, is charred in a platinum or clay crucible at a dull red heat; the charred mass is reduced to a fine powder in a porcelain mortar, mixed most intimately with 20 to 30 grams of spongy platinum, the mixture transferred in successive portions to a shallow, thin, platinum dish, and heated over a lamp with double draught. After a short time, even before the mixture is in a state of ignition, every particle of carbon begins to glimmer, and a grey layer speedily covers the surface of the black mixture. By diligent and cautious stirring with a small platinum spatula, the surface is renewed and the combustion promoted. As long as the mass contains unconsumed carbon, glimmering is observed; but when the carbon is entirely burnt, all visible incandescence ceases, even though a stronger heat be applied. When all the successive portions have been incinerated, the mass is uniformly mixed, any oxides which may have been produced are converted into anhydrous carbonates (see 1 *a*, p. 498), and the whole weighed. On deducting the weight of the platinum added, the weight of the ash is obtained. In this process of incineration, there is, however, a loss of chlorine, compare this vol. p. 497.

6. Other Methods of Incineration.

The descriptions given in 1 to 5 do not exhaust all the methods of incineration proposed and employed. GRÄGER‡ and A. MÜLLER§ add ferric oxide, whilst BECHAMP,‖ for the incineration of vegetable and animal matters which burn with difficulty, beer yeast, for example, recommends the addition of nitrate of bismuth. It is merely necessary to mention these particular methods of incineration.

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[*] Zeitschr. f. Biologie, vol. ix. part I.

[†] Zeitschr. f. anal. Chem. 12, 405.

[‡] Jahresbericht von Kopp und Will. 1859, 693.

[§] Journ. f. prakt. Chem. 80, 118.

[‖] Compt. rend. vol. 73, p. 337; Zeitschr. f. anal. Chem. 11, 332.

II. ANALYSIS OF THE ASH.

§ 285.

Before proceeding to describe the most advantageous methods for preparing the ashes of plants, it may be as well to state that the modes of incineration, 1 and 2, if they are properly carried out, those described in 1 *c* or 2 *b* especially, being entirely satisfactory, fully answer the purpose in almost all cases.

This observation seems necessary in order to explain why the following paragraph refers exclusively to ashes which contain no admixture of baryta or platinum. If methods 4 or 5 have been used, the modifications required are but trifling, and such as will readily suggest themselves.

According to their principal constituents, the ashes of plants may be classed under the following heads:

a. Ashes in which *carbonates of the alkalies and alkaline earths* predominate; such as the ashes of woods, of herbaceous plants, &c.

β. Ashes in which *phosphates of the alkalies and alkaline earths* predominate; to this class belong the ashes of nearly all kinds of seeds.

γ. Ashes in which *silicic acid* predominates; such as those of the stalks of the *Gramineæ*, of the *Equisetaceæ*, &c.

Although it is evident that this classification cannot be strictly adhered to, and that numerous examples, intermediate between two of the groups will be met with, it must be followed, if the analytical methods about to be described are used, since certain modifications of the general mode of procedure have to be made according as the ash belongs to the first, second or third class.

a. Qualitative Analysis.

As the constituents which usually occur in the ashes of all plants are known, a complete qualitative analysis, as a general rule, would be superfluous. A few preliminary experiments suffice to ascertain the presence or absence of the more rarely occurring constituents, and also, more particularly, to which of the above classes the ash belongs. These experiments are as follows:

1. *The reaction of the ash must be ascertained.*

2. *The ash is heated with concentrated hydrochloric acid, to see whether it is completely decomposed by it or not.* If the ash effervesces strongly when treated with the acid, this may be regarded as a proof that it can be decomposed. The ashes of the stalks of the *Gramineæ*, &c., which abound in silicic acid, are usually the only kind that are not completely decomposed by hydrochloric acid.

3. If, after separating the silicic acid and removing the greater part of the free acid from the hydrochloric solution of the ash, it is mixed with an alkali acetate, or neutralized with ammonia and free acetic acid added, a gelatinous yellowish-white precipitate of ferric phosphate will almost invariably separate. It is now necessary to ascertain *whether the ash contains any phosphoric acid besides that which is in this precipitate.* In order to decide this question, the precipitate thus obtained is filtered off, and ammonia in excess added to the filtrate; if *no precipitate* is formed, or if the precipitate is brownish-red, when it consists of hydrated

ferric oxide, the ash contains no more phosphoric acid; if, however, a white precipitate is produced (phosphate of lime, and phosphate of magnesia and ammonia), it is certain that the ash contains more phosphoric acid than the ferric oxide present in it can combine with, and consequently the ash must be classed under the second head.

4. *The ash is tested for manganese,* by mixing a small portion with carbonate of soda, and exposing the mixture on platinum foil to the outer flame of the blowpipe (see "Qualitative Analysis," 10th English Edition, p. 122).

5. *Sulphuretted hydrogen* is tested for in the gases evolved on treating the ash with hydrochloric acid.

6. The ash is tested for *lithia*, *rubidia*, *strontia*, *baryta*, *oxide of copper*, *alumina*, *iodine*, *bromine*, *fluorine*, and the rest of the above-named substances which occasionally occur in very small quantities, if it is considered desirable to ascertain whether traces of them are present (see "Qualitative Analysis," 10th Edition, p. 389).

b. Quantitative Analysis.

a. Ashes in which the Carbonates of the Alkalies or Alkaline Earths predominate, and in which the whole of the Phosphoric Acid may be assumed to be in combination with Ferric Oxide.

§ 286.

The determinations are made with two separate portions, which may be distinguished as AA and BB.

In BB, the carbonic acid* and the chlorine are determined.

In AA, the other constituents.

If the ash, however, contains metallic sulphides, three separate portions must be taken, the first for the carbonic acid and sulphuretted hydrogen, the second for the chlorine, and the third for the remaining constituents.

AA.

1. Determination of the Silicic Acid, Charcoal, and Sand.

4 or 5 grams of the ash is treated with water in a porcelain dish, and hydrochloric acid gradually added. If the ash abounds in carbonates, the dish should be covered with an inverted funnel, a small funnel inserted into the neck of the latter, and the acid added through this; in this way all loss from spirting is prevented. A gentle heat is applied, and as soon as the carbonic acid has been expelled, the funnels are rinsed into the dish; when no more undecomposed ash is visible, with the exception of the readily distinguishable carbonaceous and sandy particles which are almost invariably present, the whole is evaporated to dryness on the water-bath, with frequent stirring in the last stage of the process, until all the lumps are reduced to powder, any sand present being easily recognised by the grating sound produced.

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* The estimation of the carbonic acid, although, as we have seen above (this vol. p. 497), of no great value in itself, is yet necessary to complete the analysis, and thus to supply a certain control of its accuracy.

When cold, the dry mass is moistened with concentrated hydrochloric acid, and the whole, after half an hour, is heated with a moderate amount of water on the water-bath, diluted further, and the acid liquid filtered through a stout filter which has been previously dried at 110° and weighed.

The silicic acid remains upon the filter, mixed with charcoal and sand, if these are present. If the residue consists solely of silicic acid and charcoal, it is thoroughly washed,* dried at 110°, weighed, and after incineration, again weighed; this gives the *silicic acid*, the difference being *carbon.* It can be seen whether the silicic acid is pure or not by treating it with hydrofluoric and sulphuric acids. If the contents of the filter consist of silicic acid, charcoal and sand, it is transferred, after being washed and dried, from the filter to a platinum dish, without injuring the filter; this may be readily accomplished if the powder is perfectly dry, only a few particles of charcoal remaining attached to the paper, just sufficient to colour it slightly. The powder is now boiled for half an hour with a dilute solution of pure soda, free from silicic acid (or with a concentrated solution of carbonate of soda), whereby the whole of the silicic acid is gradually dissolved without affecting the sand or charcoal that may be present. The solution is now passed through the original filter, and the undissolved residue thoroughly washed, and dried with the filter at 110° until it no longer loses weight. The weight of the filter being deducted, the remainder is put down as *charcoal and sand.*

The filtrate is supersaturated with hydrochloric acid, and the *silicic acid* in it determined as directed in § 140, II. *a.*

2. Estimation of all the remaining Constituents, with the exception of Chlorine and Carbonic Acid.

The hydrochloric acid solution filtered from the silicic acid, charcoal, and sand, after being intimately mixed with the washings, is divided, by weight or measure, into three, or, more conveniently, into four parts since this will leave one part for unforeseen accidents. The best way of effecting the division, is to filter the liquid into a 200 c.c. flask or measure, to fill up to the mark with the washings and pure water, shake, and then to measure off with a pipette three portions of 50 c.c. each; these three portions may be severally designated *aa*, *bb*, and *cc*. In *aa*, the ferric phosphate is determined, any free ferric oxide or oxide of manganese present, also the alkaline earths, and any alumina if it should be present. In *bb*, the sulphuric acid; and in *cc*, the alkalies.

aa. Estimation of the Ferric Phosphate, &c., and of the Alkaline Earths.

The solution is mixed with ammonia until a permanent precipitate is formed, acetate of ammonia is added, and sufficient acetic acid to render the liquid distinctly acid; the yellowish-white precipitate, which consists of *ferric phosphate*, separates more readily if the mixture is gently warmed. It should be filtered off without loss of time. If the precipitate is small, and the ash contains no appreciable amount of manganese or alumina, and if the filtrate is not red, the precipitate is washed with hot water containing some nitrate of ammonia, heated to redness, and weighed; the ignited residue being calculated as Fe_2O_3,PO_5 (see Vol. I. p. 161). If, on the other hand—the same conditions holding good—the precipitate is larger, it is washed three or four times, dissolved in the smallest possible quantity of hydrochloric acid, ammonia added until a permanent precipitate begins to form, and then acetate of ammonia and a little free acetic acid. After gently warming, the precipitate is collected, washed, as described above, dried, ignited, and calculated as Fe_2O_3,PO_5.

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* As any considerable bulk of charcoal can only be thoroughly washed with difficulty, an ash rich in carbon cannot be accurately analyzed.

If any of the conditions above mentioned do not exist, for instance, if the precipitate is collected direct, or after being collected it is partially washed, redissolved in hydrochloric acid, and again precipitated by acetate of ammonia, the precipitate cannot be directly weighed and reckoned as Fe_2O_3,PO_5, since it may in these cases contain protoxide of manganese, and alumina, or, if the filtrate was red, basic ferric phosphate. If the latter, the precipitate can be heated to redness, weighed, dissolved in hydrochloric acid, and the *ferric oxide* determined in the solution, as in Vol. I. p. 316, *g.* β, and from the difference the amount of *phosphoric acid* combined with it can be found.

If, however, the presence of manganese, and perhaps also alumina, in the precipitate is suspected, it is dissolved in hydrochloric acid, the *iron* and *manganese* removed (which may be separated as in Vol. I. p. 316, *g.* β), or according to Vol. I. p. 437, [**82**], and the filtrate evaporated in a platinum dish with the addition of excess of pure carbonate of soda until ammonia ceases to be liberated on adding more of the carbonate; a little nitric acid is then added, and the whole evaporated to dryness and heated until it melts. The residue is dissolved in water, transferred to a small beaker, hydrochloric acid added, the whole warmed, and after being filtered, ammonia is added until the liquid is alkaline. If no precipitate is produced, alumina is absent. In that case, the solution is repeatedly evaporated with nitric acid on the water-bath, and the *phosphoric acid* estimated by the molybdenum method (Vol. I. p. 307, β). If, on the other hand, a precipitate is produced on adding ammonia, nitric acid is added until the precipitate is redissolved; the whole is evaporated repeatedly with nitric acid, and the *phosphoric acid* determined by the molybdenum method. After the molybdic acid has been precipitated from the filtrate by means of sulphuretted hydrogen, it is filtered, and the *alumina* in the filtrate determined as in Vol. I. p. 192, *a*.

If the hydrochloric solution of the fused mass gives a precipitate with ammonia, it contains alumina, and, if it is desired to avoid the inconvenient separation of the molybdic acid described above, the alumina may be determined, in the hydrochloric solution of the fused mass, as *phosphate of alumina* by adding phosphate of soda to the liquid, then ammonia, and finally acetic acid until the latter is in excess. The precipitate obtained in this way is collected, washed, dried, heated to redness, weighed, and reckoned as Al_2O_3,PO_5. In estimating the *phosphoric acid*, the last 50 c.c. of the solution filtered, after it has been freed from silicic acid, &c, is used, proceeding as described in this vol. p. 508, *a*.

In the filtrate from the ferric phosphate, after it has been rendered acid by acetic acid, the *lime* and *magnesia* are determined, also the rest of the *iron* and *manganese*,* if there is any. For this purpose the ferric oxide is precipitated, if necessary, by ammonia, or the iron and manganese (which should be separated as in Vol. I. p. 437 [**82**]) by ammonia and sulphide of ammonium, and the lime and magnesia determined as in Vol. I. p. 421 (**36**), after destroying the excess of sulphide of ammonium, if there be any, by evaporating with hydrochloric acid and filtering.

bb. Estimation of the Sulphuric Acid.

The solution *bb* is precipitated with chloride of barium, and the precipitate determined as directed in Vol. I. p. 299, 1. If the solution contains a large excess of hydrochloric acid, the latter should be partly neutralised with ammonia.

cc. Estimation of the Alkalies.

The liquid *cc* is mixed with a quantity of chloride of barium just sufficient to precipitate the sulphuric acid as estimated in *bb*, and evaporated on the water-bath until the greater part of the free acid is removed; after it has been diluted, a few drops of ferric chloride are added, then pure milk of lime in slight excess, and the whole is heated for some time on the water-bath and filtered. By this means, the whole of the sulphuric acid, phosphoric acid, ferric oxide, oxide of manganese, and magnesia is removed. The precipitate is washed until the last washings, after being acidified with nitric acid, no longer produce the least turbidity with solution of nitrate of silver; the excess of lime is precipitated from the filtrate by means of carbonate of ammonia mixed with ammonia, and the precipitate allowed to subside and filtered off. The filtrate is then evaporated to dryness in a platinum dish, ignited, redissolved, and precipitated again, and, if necessary, a third time, with ammonia and carbonate of ammonia (in fact, until the solution of the gently ignited residue is no longer rendered turbid by ammonia and carbonate of ammonia). Finally, it is evaporated, ignited gently, and the residual alkali chlorides weighed, the *soda* and *potassa*, if both alkalies are present, being separated as directed in § 152.

N.B. If the quantity of ash is small, the liquid filtered from the silicic acid may be divided into two parts only, and the sulphuric acid and alkalies determined in one, by first precipitating the sulphuric acid, avoiding any appreciable excess of chloride of barium, filtering, and then proceeding as in *cc*.

BB. Estimation of Carbonic Acid, Chlorine, and any Sulphur which may be present in the form of metallic sulphides.

1. *When the qualitative examination indicates the absence of metallic sulphides from the ash.*—In order to determine the *carbonic acid*, a second portion of the ash is treated as in Vol. I. p. 338, *bb*., or Vol. I. p. 340. The contents of the small flask in which the solution is effected

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* No reference is made in the text to the very unusual event of the liquid still containing alumina; should this happen, the solution is precipitated by ammonia or sulphide of ammonium, and the alumina separated from iron or manganese according to § 160.

by means of dilute nitric acid is filtered, and the chlorine in the filtrate precipitated by silver solution, as in Vol. I. p. 354, *a*.

2. *When the qualitative examination has shown the presence of metallic sulphides in the ash.*—A second portion of the ash is treated with hydrochloric acid, and the sulphuretted hydrogen (and in this way the *sulphur* present in the form of metallic sulphides) and *carbonic acid* evolved, are estimated as in this vol. p. 233, *d*. In order that the estimation of the sulphuretted hydrogen may be accurate, it is advisable to conduct the operation in an atmosphere of hydrogen (this vol. p. 330, *a*). To estimate the *chlorine*, a third portion of the ash is boiled with water, filtered, and the filtrate mixed with a solution of nitrate of silver in excess; the portion of the ash insoluble in water is treated with cold, dilute nitric acid, filtered, and the aqueous filtrate which has been precipitated by the silver solution is acidified with this. The whole is then left to settle, light being excluded, and the precipitate, consisting of chloride and sulphide of silver, is collected, washed, and treated with ammonia to dissolve the chloride of silver; the solution filtered from the sulphide of silver is then acidified with nitric acid, and the now pure chloride of silver estimated as in Vol. I. p. 354, *a*.

N.B. If the quantity of ash is very small, the whole of the constituents, if free from sulphides, may be determined in one and the same portion. In this case, the carbonic acid is first determined as in BB. 1, the liquid filtered through a weighed filter, the chlorine estimated in the filtrate, and the excess of silver precipitated by hydrochloric acid; the first filter is then spread on a glass plate, and the contents are rinsed off from it into the second filtrate; the rest of the process is conducted as in AA. The rinsed filter is dried, and the residual charcoal, sand, and silicic acid are subsequently again collected on it.

β. *Ashes decomposed by Hydrochloric Acid, and in which more Phosphoric Acid is present than that existing in combination with Ferric Oxide.*

§ 287.

Two portions of the ash are taken, a larger, *AA*, and a smaller, *BB*. In *BB*, the carbonic acid and chlorine are determined as in § 286; in *AA*, the other constituents. If the quantity of ash is very small, the whole of the constituents are determined in one and the same portion (see § 286, BB, "N.B.").

AA is treated with hydrochloric acid, and the silicic acid, charcoal, and sand separated as in § 286, the hydrochloric acid solution being then made up to 300 c.c., and divided into two parts, one of 100 c.c. *aa*, the other of 200 c.c. *bb*.

In *aa*, the *sulphuric acid* is first determined by adding chloride of barium in the smallest possible excess, and to the filtrate, solution of ferric chloride is then added until the liquid appears yellow; nearly the whole of the free acid is removed by evaporation on the water-bath, the residue diluted, and pure milk of lime added until the liquid has a strongly alkaline reaction. It is next heated almost to boiling, filtered, washed until the washings no longer contain chlorine, and after the lime and baryta have been removed from the filtrate by carbonate of ammonia, the *alkalies* are determined as directed in § 286.

Ammonia in slight excess is added to *bb*, then acetic acid until the precipitated phosphates of the alkaline earths are redissolved. The precipitate, which consists chiefly of ferric phosphate, but may also contain oxide of manganese, occasionally alumina, and, if the quantity is considerable, also traces of the phosphates of the alkaline earths, is treated as described in this vol. p. 504, *aa*. The filtrate is divided into two equal parts, *a* and *β*, and the *phosphoric acid* determined in one, *a*, and the *lime* and *manganese* in the other, *β*.

a. To estimate the former, the liquid is repeatedly evaporated with nitric acid, on a water-bath, almost to dryness, the residue treated with nitric acid, and the phosphoric acid determined by the molybdenum method (Vol. I. p. 307, *β*). It should be noted that, after dissolving the phosphomolybdate of ammonia in ammonia and neutralising the greater part of the ammonia by hydrochloric acid, it is useful to add a certain quantity of solution of ammonia again (4 to 6 c.c.); the magnesia mixture is then added drop by drop, and finally some more ammonia, until the latter forms one-fourth of the whole. If this method of determining the phosphoric acid is employed, accurate results are obtained with certainty, whether the ash contains salts of orthophosphoric or pyrophosphoric acid.

β. To determine the *lime* and *magnesia* in *β*, the method described in Vol. I. p. 422, (**37**) is used. If the ash contains an appreciable quantity of manganese, this must be removed from the portion *β* in which the lime and magnesia are to be determined, as it would otherwise be thrown down partly with one and partly with the other. The liquid *β*, rendered acid by acetic acid, and still containing alkali acetate, is treated with chlorine or bromine at a temperature of 50° to 60°, and the hydrated peroxide of manganese is filtered off, washed, dissolved in hydrochloric acid, and the *manganese* precipitated and estimated as manganous sulphide. The filtrate, which still contains portions of alkaline earths (Vol. I. p. 431 [**70**], *a*), is evaporated with hydrochloric acid, filtered, and the filtrate added to the filtrate from the hydrated peroxide of manganese; the lime and magnesia are then determined in the mixed filtrates in the manner previously described.

Of the large number of methods which may be chosen for the treatment of the liquid *β*, if it contains no manganese, the following only need be mentioned. After the ferric phosphate has been separated, the lime is precipitated from the acetic acid solution by oxalate of ammonia (Vol. I. p. 422 [**37**]). The filtrate is then divided into two equal parts, the magnesia determined in one, by the addition of ammonia, and phosphate of soda and ammonia, whilst in the other, after evaporation with nitric acid, the phosphoric acid is precipitated by the addition of ammonia and solution of chloride of magnesium mixed with chloride of ammonium.

γ. *Ashes not decomposed by Hydrochloric Acid.*

§ 288.

Carbonic acid is rarely found in ashes of this class, but when it is, it is determined as well as the chlorine as in § 286. As far as the estimation of the other constituents is concerned, the ash must first be submitted to a preliminary decomposition; this may be carried out in several ways.

1. It may be effected, as WILL and the author first suggested, by evaporating the ash to dryness with pure solution of soda, in a platinum or silver dish. (The results of many experiments have shown that in this way the silicates in the ash are completely decomposed, whilst the sand which may be mixed with the ash is left unacted on, or nearly so. The heat must not be raised, in the last stage of the process, sufficiently high to fuse the mass.) The residue is then treated with dilute hydrochloric acid, evaporated, treated again with more acid, and the insoluble residue dealt with (silica, charcoal, and sand), as directed in § 286 AA. 1, and the solution as in § 286 AA. 2, or § 287 AA. As the alkalies cannot be determined in this solution, they are estimated in a separate portion of the ash, which for this purpose is decomposed either by fusion with hydrate of baryta, or by hydrofluoric acid.

2. WAY and OGSTON* mix the ash (free from sand) with an equal weight of nitrate of baryta, and project it into a large platinum crucible in small portions at a time; in this way the ash is rendered easily decomposable by hydrochloric acid, and the charcoal which it may contain is burnt so that it becomes quite white. The silicic acid is separated as in § 286, AA. 1, and any sulphate of baryta which may be present is determined and allowed for. Of the hydrochloric acid solution, a portion is used for the estimation of the alkalies by the method described in § 286, AA. 2, *cc.*, and the remainder is precipitated with a slight excess of sulphuric acid. (As the quantity of nitrate of baryta used is known, the excess over the calculated weight of sulphate of baryta gives the amount of sulphate of lime which has been precipitated along with it.) The filtrate is then divided into two portions, the ferric phosphate, the lime and the manganese being determined in one (§ 287); and the phosphoric acid in the other as in § 134, *d. a.*

With regard to other methods of analysing the ashes of plants or other ash, the works of E. REICHARDT,† R. W. BUNSEN,‡ J. KÖNIG,§ and R. ULBRICHT (Analysis of the ash of must and wine)|| should be consulted.

B. Supplementary Estimations for ascertaining the presence of certain Inorganic Substances in Plants.

§ 289.

From what has been said at the beginning of § 284, it follows that although, by analysis of the ash of a plant or part of a plant, the composition of the ash—which possesses an interest of its own—can indeed be ascertained, nothing is known as to the amount of those elements which are lost more or less in the process of incineration, such as chlorine, sulphur, and in many cases phosphorus.

If therefore the amount of these substances present in the plant, or

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* Journal of the Royal Agricultural Society, VIII. Part I.

† Archiv. der Pharm. [2], 132, 88; Jahresber. von H. WILL, 1867, 831.

‡ Annal. der Oenologie, 1, 3; Zeitschr. f. anal. Chem. 9, 283.

§ Landwirthschaftl. Versuchsstationen, 10, 396; Zeitschr. f. anal. Chem. 9, 288.

|| Landwirthschaftl. Versuchsstationen, 25, 399.

portion of the plant, has to be ascertained, then the following estimations, complementary to the ash analysis, must be carried out.

1. Estimation of the Chlorine.

This is effected by moistening 10 grams of the chopped plant or of finely divided portions of the plant with a solution of about 1 gram of pure carbonate of soda and drying. It is then incinerated in a platinum dish at a moderate heat, long continued, whereby, if an incipient red heat is not exceeded, no loss of alkali chloride will take place. Directly the particles of carbon cease to glow, the ash (still containing carbon) is moistened with water, ground up, exhausted with boiling water, filtered, and the filter washed and added to the remainder of the ash in the platinum dish; the whole is now dried and incinerated completely, the ash treated with cold dilute nitric acid, filtered into the aqueous solution, more nitric acid being added if necessary, until it is in excess; the chlorine in the solution is then determined as chloride of silver, according to Vol. I. p. 354, a. (BEHAGHEL VON ADLERSKRON).* Another method of estimating the chlorine will be mentioned under 3.

2. Estimation of the Sulphur,

with which, when necessary, that of phosphorus may be combined.

a. W. KNOP *and* R. ARENDT'S *method.*†

About 4 or 5 grams of the shredded plant is drenched with the most concentrated nitric acid, evaporated to dryness on the water-bath, moistened once more with the nitric acid, and again evaporated almost to dryness; some water is now added, followed by 2 to 3 grams of pure dry carbonate of soda (which must be sufficient to neutralise all the free acid), and the whole dried, stirring at the last. The mass is then moistened with water so that it easily separates from the basin, and more water is added until the whole is of a thin pasty consistence; 20 to 25 grams of ground, dried carbonate of soda are added and the whole, after being intimately mixed, is dried completely, ground to a fine powder, and the dish, which has become damp from the vapour of water, is cleaned out with carbonate of soda. The powder is then heated, in separate portions if necessary, in a silver or platinum crucible over a spirit flame, until the mass, which must not be allowed to melt, has become quite white. If this cannot be accomplished, the substance is powdered once more, mixed with a few decigrams of nitrate of potassa, and again heated.

Finally, the mass is treated with water, supersaturated with hydrochloric acid, the silica separated, the sulphuric acid precipitated from the moderately acid liquid by chloride of barium, and the *sulphur* calculated from the sulphate of baryta, after it has been purified as in Vol. I. p. 299. If the *phosphoric acid* in the filtrate has to be determined, this is effected, according to KNOP, by the uranium method (Vol. I. p. 310), after the small amount of ferric chloride present has been reduced by protochloride of uranium.

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* Zeitschr. f. anal. Chem. 12, 395.

† Compare R. ARENDT. "Das Wachsthum der Faserpflanzen" (private communication from Herr D. G. BRÜGELMANN).

b. Any of the other methods described in §§ 188 and 189, suitable for the estimation of sulphur and phosphorus in organic substances, may be employed, preferably Liebig's (§ 188, 1). The fused mass is treated with water, the solution supersaturated with hydrochloric acid, the silica separated, and the *sulphuric acid* in the filtrate precipitated by chloride of barium. If the *phosphoric acid* has also to be estimated, this can be effected not only in the manner prescribed in *a*, but also by nearly neutralising the filtrate from the sulphate of baryta with carbonate of soda, adding a little ferric chloride, and finally a slight excess of carbonate of baryta. It is then filtered after settling, and the precipitate, containing the whole of the phosphoric acid, is washed, dissolved in nitric acid, and the phosphoric acid determined by the molybdenum method (Vol. I. p. 307, β).

3. Estimation of the Sulphuric Acid, and also, if required, the Chlorine, contained in Plants.

If the question has to be decided as to which portion of the sulphur found in 2 is contained in the plants as sulphuric acid, it is extracted with cold water containing nitric acid, as already recommended by Caillat (see this vol. p. 495, footnote). E. Wolff * advises, for this purpose, the employment of a glass tube about 60 cm. long and 1·5 to 2 cm. in diameter drawn out at one end. The drawn out open end is connected with a glass tube by means of a small caoutchouc tube furnished with a pinchcock. Cotton-wool boiled in very dilute nitric acid is now placed in the constricted part of the tube, and over it about 10 grams of the finely divided vegetable substance. The apparatus is then filled, the pinchcock being closed, with a mixture of 20 parts of water and 1 part of nitric acid of sp. gr. 1·2. After a few hours, some of the liquid is run off, so that a fresh layer of the dilute acid may come in contact with the substance to be extracted, the tube being filled up again and this treatment continued until a sample of the effluent liquid on adding silver solution exhibits a faint opalescence only. If *sulphuric acid* alone is to be estimated in the liquid, it is evaporated, preferably on the water-bath—to a small bulk—diluted with water, precipitated with chloride of barium, and the sulphate of baryta purified according to Vol. I. p. 299. If, however, *chlorine* also is to be determined in the liquid, it is first precipitated with nitrate of silver, the chloride of silver (containing organic matter) filtered off, and the excess of silver in the filtrate removed by precipitation with hydrochloric acid; the filtrate, after being evaporated until the free acid is almost entirely driven off, is diluted, and the sulphuric acid determined as above. The chloride of silver containing organic matter, after it has been washed, is dissolved in ammonia, the solution evaporated with the addition of carbonate of soda, and the residue heated until it just melts; it is then treated with water, the solution acidified with nitric acid, precipitated by silver solution, and the now pure chloride of silver determined as in Vol. I. p. 354, a. The estimations of sulphuric acid and chlorine conducted in this manner, however, generally yield incomplete results, as the plant substance can only with difficulty be completely exhausted with water containing nitric acid.

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* His "Anleitung zur chem. Untersuch. landwirthschaftlichwichtiger Stoffe," third edition, p. 167.

C. Arrangement of the Results.

§ 290.

If it is merely a question of representing the results of ash analyses, it is sufficient to state the percentages of the bases and acids separately, as the manner in which the bases and acids found were originally combined as salts in the plant cannot be inferred from the ash with any degree of certainty. If the chlorine is treated in this way, an equivalent amount of oxygen must be subtracted. The chlorine, however, is usually put down as chloride of sodium, and, if there is not enough soda, as chloride of potassium, the equivalent quantity of the alkali being subtracted from the total amount of soda and potash found. In ashes which contain carbonates of the alkaline earths, the manganese which may be present is put down as oxide (see Vol. I. p. 432), otherwise as protosesquioxide.

If the results are merely given in this way, that is to say, as they are directly obtained, they are incapable of being compared with those of other analyses, as among the constituents enumerated there are, or may be, some which are immaterial, especially charcoal and sand. Hence, if the analyses are to be comparable, they must be freed from the influence of these unessential constituents. This is done by striking out the charcoal and sand, and calculating the essential constituents into parts per 100. The carbonic acid, on the other hand, although not derived from the inorganic constituents of the plant, must be taken into account if the ash is to be characterised as such (for example, a wood-ash which is to be employed as a manure or used for making potashes).

In order to solve the question as to what inorganic substances a plant withdraws from the soil, a mere statement of the constituents is insufficient, as may be inferred from what has been said previously (this vol. p. 495); the results of the supplementary analysis must also be included, and the whole calculated to 100 parts of the dried plant.

The amounts of chlorine, sulphur, and also phosphorus were ascertained from the supplementary estimation, the other constituents from the analyses of the ash. The carbonic acid is not included in the statement of results.

In order to calculate the percentages in which the several constituents of the ash are present in the original vegetable substance, the way formerly adopted was to incinerate, with proper precautions, a small weighed portion of the carefully dried vegetable substance, and determine the total amount of the ash; then to incinerate a large unweighed portion, less carefully dried, and analyse the ash obtained. A simple calculation sufficed to find the percentages of the several constituents in the plant. For instance, a sample of wheat on incineration left 3 per cent. of ash, containing 50 per cent. of phosphoric acid; this gives 1·5 per cent. of phosphoric acid in the wheat.

This method is evidently very convenient; but it should be noted that it does not give sufficiently accurate results in all cases, since, for the reasons stated in § 284, the total amount of the ash is by no means constant, but varies more or less, within certain limits, according to the manner of conducting, intensity, and duration of the ignition. As we can, therefore, in most cases, never be sure that the smaller portion obtained in the determination of the total weight of the ash, corresponds exactly in amount and composition with the larger portion used in the analysis, it is always preferable, as already recommended, to weigh, on the one hand, the total quantity of the (dried) substance intended for incineration, and, on the other hand, the total amount of ash obtained and intended for analysis.

If it is thought desirable to avoid this, the end in view may also be attained with certainty in another manner, namely, by first incinerating a large unweighed portion of the vegetable substance, analysing the ash, and thus determining the relative proportions of the constituents; then incinerating a smaller weighed portion, previously dried at 100°, and determining in the ash one of the constituents which is not liable to undergo any change in quantity from the mode of incineration, *lime* for instance. As we know the relative quantity of this substance in the plant as well as in the other constituents of the ash, it is easy from this to calculate the percentages in which these other constituents are present in the plant.

IV. ANALYSIS OF SOILS.

§ 291.

Apart from the circumstances of climate, the fertility of a soil depends on its chemical as well as on its mechanical and physical nature. The chemical nature again is dependent not only on the nature and relative proportions of the constituents, but also on their solubility and their state of combination.

Hence, if an analysis is to afford a criterion of the fertility of a soil, all the above points must, as far as possible, be taken into consideration; advisedly as far as possible, for in a laboratory, solvents cannot be induced to act in exactly the same way as they do in nature; and again, the chemico-physical examination is scarcely sufficient to reveal the variations of the mode in which the materials are combined in the soil. That these variations do exist is evident, for instance, from the fact that a perfectly uncultivated soil, although it contains the materials necessary for a particular plant, will yet sometimes fail to support it, although it is capable of sustaining other plants of equal or even greater material requirements. The combination of the materials is, therefore, the resistance which the soil offers to the delivery of certain constituents to the plants, a resistance which, overcome by some plants, baffles the attempts of others, and which, as experiments have shown, diminishes with cultivation.*

In conformity with the object and scope of the present work, the author fully describes the mechanical and chemical analysis, but as regards the investigation of the most important physical properties of soils, the reader is referred to works on Agricultural Chemistry and the numerous papers on the subject.†

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* Comp. v. LIEBIG, The Natural Laws of Husbandry, ed. by Dr. BLYTH (Walton and Maberly, 1863), p. 65 *et seq.*

† More or less comprehensive information as to the examination of the physical conditions of soil is given by older writers, SCHÜBLER (Grundsätze der Agriculturchemie, pt. ii), and Fr. SCHULZE (Journ. f. prakt. Chem. 47, 241), and, among later authors, Dr. EMIL WOLFF'S sketch of soil analysis, reported by the members of the commission (Dr. BRETSCHNEIDER, Dr. GROUVEN, Dr. KNOP, Dr.

A. Collection of the Sample.

§ 292.

The upper layer which is broken up by the plough to a depth of about 30 cm. may be considered as surface soil; the next inferior layer to a depth of 60 cm. may be taken as the subsoil. If either surface soil, or subsoil is to be taken from a particular spot, a quadrangular hole is dug from 30 to 50 cm. square, with perpendicular sides, and bottom as nearly horizontal as possible, and a *vertical* slice of *uniform thickness* is then cut away from one side for the sample. The sample of subsoil should be taken in exactly the same way. If the sample is to be a fair average representative of the soil in a whole field, portions are taken in a similar manner from various parts and uniformly mixed. The specimens should be dried thoroughly in the air; in summer this may be done by placing the earth in a shallow box in a dry room or granary, whilst in winter it should be dried slowly in a drying closet, at a temperature of 30° to 50°.

To make a complete analysis, about 5 kilograms of soil will be required.

B. Mechanical Analysis.

§ 293.

1. The whole of the air-dried earth is weighed, and the *stones* picked out, brushed, and weighed.

2. The earth is now put on to a tin-plate drum-sieve with holes 3 mm. in diameter, and sifted, as long as anything passes through. The lumps left behind, after being reduced in a mortar, using moderate pressure, preferably with a wooden pestle, are again sifted, the portion which has passed through being preserved. The sieve is now placed in a dish, water * added sufficient to cover the contents of the sieve, which after being allowed to remain for a considerable time are washed with the hand or a brush, until all the clay is removed from the small stones. Finally the latter are rinsed with a little water, transferred to a dish, dried at 125° and weighed. The weighed matter is *gravel*. If the dried gravel is ignited with free access of air, the loss of weight will indicate the organic matter belonging

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Peters, Dr. Stohmann, and Dr. Zöller), appointed at the meeting of German Agricultural Chemists in 1863 (Landwirthschaftl. Versuchsstationen, 1864, vol. vi.; Zeitschr. f. anal. Chem. 3, 85); further, E. Wolff's "Anleitung zur chemischen Untersuchung landwirthschaftl. wichtiger Stoffe," 3rd edn. (Berlin: Wiegand, Hempel and Parey, 1875); also E. Heiden's "Denkschrift zur Feier des 25-jahrigen Bestehend der agriculturchemischen Versuchsstation Pommritz," p. 152 *et seq.* (Hanover: P. Cohen, 1883). Special reference to the absorptive power of soils and the methods of determining the same is made in the papers by Liebig (Ann. d. Chem. u. Pharm. 105, 113); A. Salomon (Landw. Versuchsstat. 9, 351); R. Biedermann (*ibid.* 11, 1); Cl. Treutler (*ibid.* 14, 301); W. Knop (Zeitschr. f. anal. Chem. 13, 101; 14, 241; 15, 171); W. Pillitz (*ibid.* 14, 55, and 282): A. Lissauer (Landw. Versuchsst. 19, 11); Van Bemmelen (*ibid.* 21, 135, and 23, 265); König (*ibid.* 26, 400); and, concerning the retention of water by the soil, the treatises by F. Seelheim (Zeitschr. f. anal. Chem. 19, 387); H. Fleck (Dingl. polyt. Journ. 238, 93); Armsby (Landwirthsch. Versuchsstat. 21, 397); and Heiden (*ibid.* 26, 407).

* Distilled water must be used for all these operations; see note, p. 517.

to it, provided it consists of such small stones and rock-fragments as lose neither water, carbonic acid, nor other volatile constituents on ignition. The contents of the dish containing the earth washed away from the gravel are slowly dried, finally at 30 to 50°, the residue is mixed uniformly with what passed through the sieve before, the mixture spread out in as thin a layer as possible, kept for some days at a moderate temperature in a place free from vapours and dust, and the *air-dried fine earth* (thus named by E. Wolff) thus obtained is then preserved in a well-stoppered bottle.

It may be mentioned here, however, that a definition of the fine soil—which can, of course, only be determined by agreement and not in a scientific manner—has not yet been decided on. Whilst, for example, in accordance with E. Wolff's suggestion, which has been followed by many other Agricultural Chemists, that portion of the soil passing through a sieve of 3 mm. aperture is designated "fine soil," others select 2 mm., and not a few, still finer sieves, for obtaining the "fine soil." Heiden (Denkschrift. p. 119), and Grandeau [*] take 1 mm.; E. Dietrich,[†] 0·66 mm.; A. Müller,[‡] as also Knop, 0·2 to 0·3 mm.[§] Thus it is easy to see that a comparison of the analyses of "fine soil," which is not further characterised, may lead to erroneous conceptions, the analyses being really only comparable when the "fine soils" are of identical gauge.

In the following pages, by "*fine soil*" is understood that which is in accord with Wolff's definition, the methods of analysis being of course applicable to all other descriptions of "fine soil."

3. Many very different methods have been proposed and employed for *the further mechanical separation of the air-dried "fine soil."* Many Agricultural Chemists advise elutriation and separation of the residual sand into different grades by passing it through sieves of various gauges. Others sift first, and separate by elutriation only the finest sifted portion. In sifting, however, the gauges recommended vary, and for elutriation some prefer so-called flushing apparatus, and others settling apparatus. It may readily occur, therefore, that the results obtained by the different methods are not precisely concordant. The difficulty of comparing the results thus obtained is made still more difficult by the circumstance that the names given to the sand of different degrees of fineness vary, such, for instance, as "fine gravel," "coarser sand," "finer sand," "argillaceous sand, or finer gravel," "pearl sand," "fine sand, or coarse gravel," "medium gravel," "fine gravel," "coarse sand," "fine sand," &c. &c.

The causes just enumerated as giving rise to non-concordant results in the mechanical separation of the constituents of a "fine soil," whereby the amount of clay found is too high, and often much too high, are, however, by no means exhausted. The more common source of error in the usual methods is rather that, in all elutriations carried out in the ordinary way, the clay in the soil is not obtained pure, but rather mingled with fine sand, and, under some circumstances, with finely divided carbonate of lime (Schlösing,* Grandeau,† F. Sestini,‡ N. Pellegrini§).

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[*] His "Handl. f. Agriculturchem. Analysen," German edn. by Henneberg (Wiegand, Hempel and Parey, Berlin, 1879), p. 103.

[†] Zeitschr. f. anal. Chem. 5, 298.

[‡] *Ibid.* 5, 443.

[§] According to A. Mayer, the largest particles of Knop's "fine soil" were 0·3 mm. diameter (Böckmann, Chem. techn. Untersuchung (J. Springer, Berlin, 1884), 2, 664).

It is not here necessary to notice all the methods of mechanical analysis which have been proposed. It suffices to describe the following.

a. One of the best purely mechanical methods is W. Knop's as modified by E. Wolff.‖

b. Schlösing's method, which combines mechanical separation with chemical treatment; this, as far as our present experience goes, is the only process which gives correctly the amount of alumina existing in the soil.

a. Purely Mechanical Method.

§ 294.

Among numerous methods, E. Wolff's modification of Knop's process is quoted here, as it gives, with very simple apparatus, as good results as can be expected from a purely mechanical analysis. As regards the other processes, the original treatises and books mentioned in the footnote¶ may be consulted.

50 grams of the air-dried "fine earth," after being boiled with distilled water for a long time, is introduced into a sieve of perforated brass, with holes of 1 mm. in diameter, so placed in a basin of water that its contents are covered, operating in the manner described above, in order to separate the portions of more than 1 mm. diameter from the finer parts. It is then treated in a similar manner, using a sieve of 0·5 mm. gauge, and, lastly, one of 0·25 mm. gauge, the portions remaining in the sieves being treated as already described for the gravel. Where many analyses of earth have to be made, it is advisable to use an apparatus in which the sieves of different gauges fit one over the other, the whole forming a system which is suspended in a deep, wide glass vessel filled with water. The sieves, whose contents are kept moving by revolving brushes, then work simultaneously and the operation is greatly facilitated.

The further separation of the portion coming through the last sieve, into fine sand and the finest elutriable portions (called "dust" by E. Wolff), is effected by an elutriating flask holding fully one litre, and about 20 cm. high, in the neck of which, through a hole in the cork, a syphon can be inserted, the shorter limb of which reaches to the bottom of the flask and is bent upwards at the lower end. The substance which has passed through the finest sieve is introduced into the flask, which is then filled to a height of about 18 cm. with distilled water,* well shaken, and left for a certain time. The syphon is then inserted, and the turbid liquid drawn off from the sediment; more distilled water is poured in, and the whole shaken again and the operation repeated. WOLFF recommends that it should be left to settle for one hour after the first shaking, then for ½ hour, ¼ hour, and lastly 5 minutes, repeating the operation three times for each time of settling. Finally, the fine sand is rinsed out into a basin and treated in the same way as the other sands.

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* Compt. rend., 78, 1276.

† His "Handbuch," p. 104.

‡ Landwirthschaftl. Versuchsstat. 25, 47.

§ *Ibid.* 25, 48.

‖ His "Anleitung zur chem. Untersuchung. landwirthschaftlich. wichtiger Stoffe," 3rd edn. p. 9.

¶ Of the apparatus for elutriation belonging to the *flushing system* those of Schulze and Schöne have already been mentioned in Vol. II. pp. 265, 266. Others belonging to the same category are described by Nöbel (see E. Wolff's treatise in Zeitschr. f. anal. Chem. 3, 90, and in Landwirthschaftl. Versuchsstat. 8, 408); E. Dietrich (Zeitschr. f. anal. Chem. 5, 295); and Al. Müller (*ibid.* 16, 83). Slight modifications of Schöne's apparatus have been recommended by E. Heiden (Denkschrift, p. 121); and C. Holthof (Zeitschr. f. anal. Chem. 25, 34). Moreover, *sedimentary apparatus* have been constructed by Knop (his "Bonitirung der Ackererde," 2 edn. p 50 *et seq.*); J. Kühn (Böckmann's "Chem. techn. Untersuchungen" (J. Springer, Berlin), 2, 665); R. Deetz (Zeitschr. f. anal. Chem. 15, 428).

To obtain and estimate the finest elutriated portions, the turbid washings are united and warmed in a large basin until they have cleared completely; the clear liquid is then drawn off by a syphon, as far as possible, and the precipitate is rinsed into a porcelain basin, and dried in it; the residue is then transferred to a platinum dish or porcelain crucible, dried at 125°, weighed, ignited with access of air, and reweighed.

To facilitate the separation of the finest elutriable particles from the water used, A. MÜLLER † recommends the addition of ammonia soap, whilst Fr. SCHULZE advises the use of carbonate of ammonia. According to E. LAUFER,‡ however, neither of these leads to satisfactory results, although he considers that warming the water greatly assists the clarifying process. See, however, A. MÜLLER'S§ criticism of this. If the component portions of the air-dried fine soil, obtained in this way, are calculated in percentage, and added together, they give not 100 but less, the difference being equivalent to the moisture contained in the fine soil. These results can be checked by using the direct method of estimating moisture given in § 296, 1. If the direct determination of the finest elutriable portion has been omitted, but the direct estimation of moisture carried out at 125°, then the amount of the former may be ascertained by deducting from 100 the sum of the fine sand dried at 125° and the moisture.

As the moisture in different kinds of fine soil may vary very greatly, it is advisable, for purposes of comparison, to refer the figures obtained to the substance dried at 125°. The results of the purely mechanical analysis may be conveniently set out as follows:—

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* The process cannot be carried out with spring water, as the slightest traces of salts of lime, magnesia, and alkalies cause the clay to coagulate to a certain extent, so that it goes down along with the sand (SCHLÖSING, also GRANDEAU'S Handbuch, p. 105).

† Zeitschr. f. anal. Chem. 5,243.

‡ Landwirthschaftl. Versuchsstation. 18, 61; Zeitschr. f. anal. Chem. 14, 398.

§ Landwirthschaftl. Versuchsstation. 24, 65.

100 parts of the fine earth dried at 125° contain (for example)

		Fixed matter.	Combustible or volatile matter.
7·51	Sand of 1 to 3 mm. in diameter	6·91	
	Organic substances, &c., belonging thereto		0·60
30·96	Sand of 0·5 to 1·0 mm. in diameter	30·05	
	Organic substances, &c., belonging thereto		0·91
32·71	Sand of 0·25 = 0·5 mm. in diameter	31·61	
	Organic substances, &c., belonging thereto		1·10
17·63	Sand of less than 0·25 mm. in diameter	16·77	
	Organic substances, &c., belonging thereto		0·87
11·19	Finest particles	10·36	
	Organic substances, &c., belonging thereto		0·82
100·00		95·70	4·30

7·16 Gravel associated with 100 parts of the fine earth dried at 125°.
2·10 Stones ,, ,, ,, ,, ,, ,,
5·03 Moisture belonging to 100 parts of the fine earth dried at 125° (in air-dried condition).

The loss which the soil, dried at 125°, undergoes on ignition with access of air, cannot be considered as combustible organic matter merely, since the clay, dried at 125°, gives up water when heated to redness, calcareous sand loses carbonic acid, and so on. The carbonic acid evolved can in great part be restored to the residue by moistening with a solution of carbonate of ammonia, then drying, repeating this treatment several times, and finally igniting it very gently: see § 296, 2. The figures for organic matter obtained in this way are, however, always approximate only, being near the truth in many soils, but diverging widely from it in others, as may be seen from numerous analyses of soils, those by G. Loges for example.*

b. Schlösing's *Method.*†

§ 295.

This has for its object the determination of the following constituents of fine soil:

1. Sand insoluble in acids.
2. Clay.
3. Humic substances.
4. Carbonate of lime.
5. Moisture.

10 grams of air-dried, fine soil, in a porcelain dish, are made into a stiff paste by spirting in a small quantity of distilled water; more water is then added and uniformly and thoroughly incorporated with the soil by the use of the fingers. The turbid liquid, after adding more distilled water, is now poured into a beaker holding 250–300 c.c. until the whole mass of soil is thoroughly separated and elutriated; the amount of water should be so adjusted that the total quantity of

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* Landwirthschaftl. Versuchsstationen, 28, 238.

† Compt. rend. 78, 1276; Grandeau's "Handbuch," p. 105.

liquid does not exceed 200–250 c.c. Hydrochloric acid is now added drop by drop until the carbonate of lime is completely dissolved, the humate of lime being at the same time decomposed, and in the case of soils rich in lime, assisting the action by gentle warming. After the liquid has become clear, the solution is separated from the precipitate by decantation and filtration, finally bringing the residue on the filter and thoroughly washing it. When a direct estimation of the *lime* is desired, this can be effected in the filtrate by the process described in § 298, *a*.

The contents of the filter are now washed back again into the beaker by the use of small quantities of water, 0·5 gram of caustic potassa or 2–3 c.c. of solution of ammonia being added and allowed to act for 4–5 hours with frequent stirring, so as to bring into solution the particles of humus adhering to the clay. The beaker is now nearly filled with distilled water, well stirred, left for 24 hours,* and the liquid above the sandy sediment drawn off into a 1·5 litre flask by a syphon; the liquid drawn off is replaced by distilled water, the whole stirred up, left for another 24 hours, and the process repeated some six times,† until the supernatant liquid appears perfectly clear. The 1·5 litre flask now contains the clay and humous matter, the latter in alkaline solution, whilst the beaker holds the *sand*, which may be graded as in § 294.

To the liquid containing the clay, 5 to 10 grams of chloride of potassium is added to facilitate the subsidence of the clay, and after the liquid has become clear, as much as possible is syphoned off, and decanted through a filter; finally, all the clay is brought on to the filter and washed with distilled water until the last quantity added no longer runs off through the filter, which is the case when it no longer contains chloride of potassium.

The clear water is now syphoned off from the clay, which adheres firmly to the filter, the latter being spread out on blotting-paper until the clay can be loosened, when it is transferred to a tared platinum dish, dried at 150° and weighed. Should any be left on the filter, the latter is incinerated, and the residue united with the bulk of the *clay*.

To the coloured liquid from which the clay has been separated, acetic acid is added until it is decidedly acid; it is then boiled until all the carbonic acid is removed, precipitated with acetate of lead until the supernatant liquid is colourless, allowed to subside, decanted, filtered and washed; it is then dried somewhat, the precipitate removed from the filter, dried at 100° and weighed. It is now carefully heated with access of air, any reduced lead being oxidised with nitrate of ammonia, and the residue weighed and deducted from the weight of the humate of lead, the difference being reckoned as *humic matter*.

Finally, to determine the *moisture*, a separate sample of the air-dried fine earth is dried at 150° until the weight is constant.

C. Chemical Analysis.

§ 296.

If the soil were treated as a whole in the chemical analysis, merely ascertaining the total percentages of potash, lime, phosphoric acid, silica, alumina, &c., the results could soon be obtained, but they would not give any idea of the solubilities of the several constituents. Were we, on the other hand, to treat the soil successively, with various solvents; for example, first pure water, then water containing carbonic acid and ammonia salts, then cold hydrochloric acid, then boiling hydrochloric acid, and lastly concentrated sulphuric acid, some idea of the relative solubilities of the constituents of the soil would indeed be obtained, but the analysis would then become extremely complicated, and involve an extraordinary expenditure of labour and time. When, moreover, it is remembered that the power of the soil to retain some substances more firmly than others, impedes the complete extraction of the matters soluble in a given weak solvent, there must necessarily be some uncertainty regarding the best mode of carrying out the chemical analysis of a soil.

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* According to Sestini (Landwirthschaftl. Versuchsstationen, 25, p. 47), twelve hours are sufficient.

† Sestini considers twelve repetitions necessary.

It is perfectly plain that analyses of soils cannot be comparable one with another, if they are made with the use of different sets of solvents; consequently if the analyses of soils are to be of any real value, the use of certain definite solvents must be adopted. Unfortunately, however, our knowledge is as yet insufficient to enable us to decide the question with certainty as to what analytical treatment will afford the most useful practical results, that is, give results which, when viewed in conjunction with the agricultural experiments made on the same soil, will lead to the clearest and surest conclusions; from this it follows, as a matter of course, that the views of chemists are, as yet, divided with respect to which solvents are the most appropriate.

As none of the many methods proposed for treating the earth with solvents have been universally accepted, or can be considered as generally agreed upon, it has been thought best, in the following sections, to describe the method of conducting the analysis which in the First Edition of this work appeared to the author to be the most suitable; for this, although it has naturally been improved by taking advantage of the experience acquired in the meantime, still seems to be the best adapted for practical purposes.

If, for some special purpose, it is desired to make the examination more extended, and the behaviour of the soil towards other solvents is to be ascertained—for instance, with water containing carbonic acid or ammonia—this can be done without any special directions, as the preparation of these extracts and the estimation of the dissolved constituents can be carried out substantially in the manner described for the aqueous extract.

1. Determination of the Moisture.

3 to 5 grams of the air-dried fine earth is weighed out in a platinum crucible or dish, dried at 125° until the weight is constant, and the loss of weight determined.

2. Determination of the Chemically-combined Water.

The soil, dried at 125°, is heated to redness with free access of air until constant in weight, at first over a lamp, finally over the blow-pipe. A loss in weight results from the expulsion of chemically-combined water, of carbonic and nitric acid, ammonia compounds, and combustible organic matter, both humic and of other kinds; on the other hand, an increase in weight may occur under certain circumstances, due to absorption of oxygen by compounds of the protoxides of iron and of manganese, or metallic sulphides. The water of combination, therefore, can only be estimated from the loss in weight on heating to redness in air, when all the other substances which may affect the increase or loss of weight have been determined. Even then, the amount found can only be approximately correct, as many of the factors which influence the results cannot be exactly determined.

3. Estimation of the Substances which are soluble in Water.*

§ 297.

For the preparation of the aqueous extract, one of the following methods may be selected:

a. As much fine soil as will contain 1000 grams of soil dried at 125°, is weighed out into a flask holding about 6 litres, and sufficient distilled water † is added to it to make up 5000 c.c., including that contained in the weighed soil and removable at 125°, and the height of the liquid in the flask is marked by a gummed strip of paper or some similar plan.‡ After the water has been left in contact with the soil for three days, with frequent shakings or rolling of the flask, it is allowed to settle, the almost clear liquid syphoned off into another flask, and allowed to remain another two days; it is then again syphoned off, and filtered if necessary. 1000 c.c. of the liquid thus obtained contain the ingredients extractable by water from 200 grams of the soil dried at 125°, and this, on an average, amounts to 0·1 to 0·15 gram.

β. FR. SCHULZE'S *Method.*—For this process of extraction, a three-necked WOULF'S bottle of about 2 litres capacity is required, fitted with a tubulure in one side near the bottom. A wide glass cylinder open above and contracted below is fitted air-tight into the middle neck. In this, after first introducing a loose plug of sponge into the lower contracted part of the cylinder, is placed as much fine soil as will leave 1000 grams after drying at 125°; this is covered with sifted clean gravel, and on this again so much washed fine sand that a small portion of the wider part of the cylinder may be filled with it. In one of the other two necks, a tube connected with an air-pump is fitted; the other, as well as the one at the side, being closed. The soil after being moistened with water, adding more from time to time, is allowed to remain for 24 hours; the air in the flask is then exhausted, the water laden with the soluble constituents of the soil being thus caused to run rapidly off. When the flask is nearly full, the third neck is opened and

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[*] See, in this connection, the note in the author's "Anleitung zur qualitativen Chemischen Analyse," 15th edn. p. 435.

[†] E. WOLFF advises saturating one-fourth of the water with carbonic acid.

[‡] This mark is only required when, after removal of the first aqueous extract, it is desired to prepare a second, third, &c., with an equal bulk of water, in order to determine their constituents, which is considered to be of value by some agricultural chemists (see E. WOLFF'S "Anleitung zur chemischen Untersuchung. Landwirthschaftlich wichtigen Stoffe," 3rd edn. p. 25). A soil cannot be completely exhausted even by frequently repeated extractions with water, partly on account of its absorptive power for many substances, and partly owing to the gradual but continuous decomposition of its organic matter. (Compare A. COSSA, Zeitschr. f. anal. Chem. 5, 162).

the liquid withdrawn through the aperture in the side.* The aqueous extract thus produced is perfectly clear. As a rule it is sufficient to continue the extraction until 5 litres of extract are obtained. By proceeding in this manner, the solution from *β* is of equal strength with that obtained in *a*.

The following substances are contained in the aqueous extract, and may be determined when it is considered necessary, and the amount is not too small. Potassa, soda, ammonia, lime, magnesia, ferric oxide (perhaps also ferrous oxide), sulphuric, phosphoric, and nitric acids, chlorine, silicic acid, occasionally carbonic acid, and humic substances. The estimation of these may be conveniently carried out as follows:

a. 2000 c.c. of the solution is evaporated in a platinum dish, and the residue dried at 125° and weighed, noting the weight as "*total amount of constituents soluble in water*." The residue is then ignited gently for some time with access of air, moistened with a concentrated solution of carbonate of ammonia, evaporated, gently ignited, and weighed. The loss in weight arises from the combustion of organic matter and the evolution of nitric acid and of ammonia compounds; on deducting the weight of the two latter from the total loss, the difference gives the amount of *humic substances*. Water is added to the residue and some hydrochloric acid, and the whole, after being transferred to a porcelain dish and a little nitric acid added, is evaporated to dryness, taken up again with hydrochloric acid and water, and filtered. *Silicic acid* is left on the filter, sometimes mixed with a little carbon, which may be removed, however, by burning.† The hydrochloric solution is now divided into two equal parts, *a* and *β*, and ammonia is added to *a* until it is alkaline, then acetic acid in slight excess; some drops of a dilute solution of ferric chloride are then added so as to colour the liquid red, and the whole is heated to boiling and filtered. The precipitate, after being washed, is dissolved in hydrochloric acid, the solution evaporated with nitric acid and the *phosphoric acid* estimated by the molybdenum method (this vol. p. 507). From the liquid filtered off from the basic ferric phosphate, the *lime* is precipitated as oxalate by oxalate of ammonia, and to the filtrate from this, phosphate of ammonia is added to precipitate the *magnesia* (Vol. I. p. 422 [**37**]).

Ammonia is also added to *β* until alkaline, followed by acetic acid in slight excess, and, if the liquid is reddish, the whole is heated to boiling and filtered. This precipitate contains all the *ferric oxide*. To estimate this, it is dissolved in hydrochloric acid after washing, tartaric acid, then ammonia and sulphide of ammonium are added, and it is allowed to settle; it is then filtered, and the sulphide of iron converted into ferric oxide and weighed as such (Vol. I. p. 222, b). (Should the ferric oxide precipitate also contain alumina, it must be treated as in this vol. p. 505.)

From the filtrate from the ferric phosphate, the *sulphuric acid* is precipitated by a little chloride of barium, the filtrate evaporated to dryness, and the ammonia salts removed by ignition; water is then added, and after the magnesia has been precipitated by adding a very small quantity of milk of lime the pure alkali chlorides are obtained, and the *potassium* and *soda* estimated as in this vol. p. 155. Should the composition of that portion of the soil soluble in water render it likely that sulphuric acid may be driven off or reduced on igniting the residue left on evaporation, the sulphuric acid must be estimated in a separate sample of the aqueous solution, as in § 205, 2.

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* In default of a lower tubulure, the flask is emptied by a syphon.

† If the aqueous extract was not quite clear, the silicic acid thus obtained is mixed with clay, and must be separated from it by boiling with a solution of carbonate of soda. (See this vol. p. 260, *b*.)

b. 1000 c.c. of the solution is evaporated to dryness in a not too large porcelain dish, any carbonates, and consequently any combined carbonic acid which may possibly be present, being determined by means of decinormal nitric acid and decinormal soda solution (free from metallic chlorides) as in this vol. p. 213, using an indicator free from chlorine compounds (such as phenolphthalein, this vol. p. 200); some pure carbonate of soda is then added, the whole evaporated to dryness, and agitated gently; the residue is treated with water, the solution filtered, acidified with nitric acid and the *chlorine* determined by precipitation with nitrate of silver (Vol. I. p. 354, *a*).

c. Nitric acid (also nitrous acid when present) and *ammonia*, should these exist in the aqueous solution in weighable quantities, are estimated in other portions of the solution by the methods prescribed for the analysis of natural waters (this vol. pp. 116 and 130). Of course also some of the methods mentioned in § 149 can be employed for estimating the nitric acid, particularly those which can be carried out in the presence of organic substances and also yield sufficiently accurate results even when very small quantities of the acid are to be determined. For a description of other methods for the estimation of nitric acid, reference may be made to Appendix V., Analysis of Manures.

4. Estimation of the Substances soluble in Hydrochloric Acid.*

§ 298.

As much air-dried fine soil is weighed out as will contain 100 grams of the soil dried at 125°, and 50 c.c. of water is poured on to it in a 400–500 c.c. flask, mixing uniformly; it is then heated on a water-bath, and hydrochloric acid of sp. gr. 1·149, corresponding with 30 per cent. of hydrogen chloride, is added in portions of 2 c.c. each, gradually and with shaking, until no further frothing, due to the evolution of carbonic acid, is produced on adding the last portion.† This liquid (water and the hydrochloric acid which has been added) is now mixed with an equal volume of the hydrochloric acid mentioned above, and the flask is heated for about five hours on the water-bath with frequent shaking; the contents are then transferred to a weighed porcelain dish, rinsed out with water, 10 c.c. of nitric acid (1·2 sp. gr.) added, and the whole evaporated to dryness on the water-bath. 50 c.c. of hydrochloric acid of sp. gr. 1·10, corresponding with 20 per cent. of hydrogen chloride, is now added, and the mixture, after being allowed to remain for an hour, is heated for another hour on the water-bath; about 200 c.c. of water is then added and the solution separated from the insoluble portion by decantation through a filter and thoroughly washing the residue, the filtrate being collected in a marked litre flask. If it is seen that the filtrate and washings together will make up more than a litre, the last washings are collected apart, concentrated by evaporation, and transferred to the litre flask, whose contents—after filling up to the mark—are thoroughly mixed by shaking.

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* The following inorganic substances pass into solution in hydrochloric acid: oxides and hydrated oxides, bases of the carbonates, phosphates, sulphates, and the bases of silicates decomposable by hydrochloric acid, together with a little of the silicic from them.

† Should the mass froth to such an extent that running over may be feared, a few drops of spirits of wine will stop the frothing.

The filter is spread out on a glass plate, its contents washed into the dish containing the bulk of the insoluble matter, evaporated to dryness on a water-bath, and the dish and contents are weighed; in this way the relative weights of the undissolved residue and the fine soil originally weighed out are ascertained. It is then ground up so as to mix it thoroughly, the powder uniformly mixed is placed in a stoppered glass, and heated as in 5. The hydrochloric solution, made up to 1 litre, however, is treated as follows: *

a. 300 c.c. of the solution, corresponding with 30 grams of fine soil dried at 125°, is employed for the estimation of the ferric oxide,† alumina, manganese, lime, and magnesia, for which purpose one of the methods described in § 161 is employed, usually § 161, 2. As the presence of phosphoric acid and silicic acid necessitates a few slight modifications, and some additions are necessary in view of the manganese estimation, a short sketch of the process will again be given here.

After the excess of acid has been removed by evaporation, the solution is made almost neutral with carbonate of soda, and precipitated with acetate of soda, Vol. I. p. 439 (85). The washed precipitate is dissolved in hydrochloric acid, filtered, any silicic acid remaining undissolved is determined, and the filtrate, after it has been united with the hydrochloric solution from the secondary precipitation of alumina, as will be mentioned below, is divided into two equal parts; in one of these, the *iron* is estimated either gravimetrically, Vol. I. p. 435 (77), or volumetrically, Vol. I. p. 225 *b*, *a*, and in the other the ferric oxide and the alumina, together with the phosphoric acid and some silicic acid, is precipitated with ammonia, and the precipitate ignited and weighed. The latter is fused with acid sulphate of potassa, and then treated with hydrochloric acid and water, in order to determine the small amount of silicic acid present. By deducting this, also the phosphoric acid found by *b*, and the ferric oxide, from the weight of the precipitate thrown down by ammonia, the amount of alumina is ascertained.

The filtrate from the precipitate thrown by acetate of soda is acidified with hydrochloric acid, and ammonia added until just alkaline; the slight precipitate of alumina which is thus usually produced is collected, washed and dissolved in hydrochloric acid (if this had still contained manganese, another precipitation, avoiding any appreciable excess of ammonia, would have been necessary), and this hydrochloric solution of the alumina is added to the hydrochloric solution of the precipitate produced by acetate of soda, as detailed above.

From the solution which remained clear on addition of ammonia, or has been filtered from the alumina precipitate, the *manganese* is thrown down by sulphide of ammonium (Vol. I. p. 204, *a*) or by bromine and ammonia, the latter method being preferable for small quantities of manganese. To effect this, brominated hydrochloric acid is added to the liquid until it acquires a yellow tinge, then ammonia until alkaline, and the whole heated to boiling. The brown precipitate of hydrated peroxide of manganese thus produced cannot be straightway ignited and weighed, as it contains alkaline earths. It should, after collecting and washing, be dissolved in a little hot hydrochloric acid; this solution, after dilution, being precipitated with ammonia and sulphide of ammonium in a small flask, and the manganese weighed as protosulphide. The filtrate from this is acidified with hydrochloric acid, evaporated to dryness along with the filtrate from the hydrated peroxide of manganese, the ammonia salts removed by ignition, and the *lime* and *magnesia* in the residue determined as in Vol. I. p. 421. (If the manganese was previously precipitated as sulphide, the filtrate from this is acidified with hydrochloric acid and treated in the same way.)

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* For an essentially different method of treating the hydrochloric solution see P. Latschinow, Zeitschr. f. anal. Chem. 7, 211.

† When ferrous oxide is present, a separate portion of the fine soil must be extracted by heating it with dilute hydrochloric acid in a current of carbonic acid, and the ferrous oxide in the solution estimated as in Vol. I. p. 219, *b*. By deducting the ferrous oxide from the total iron found above (reckoned to equal quantities of the fine soil), the amount of iron present as ferric oxide is ascertained.

b. 300 c.c. of the solution, corresponding with 30 grams of fine soil dried at 125°, is employed for the estimation of *phosphoric acid*,* the process given in this vol. p. 311, 10, being employed.

c. 300 c.c., corresponding with 30 grams of fine soil dried at 125°, serve for the estimation of sulphuric acid and the alkalies. With this object, the greater part of the free acid is removed by evaporation, the liquid diluted, and the *sulphuric acid* precipitated by the addition of a slight excess of chloride of barium solution to the hot liquid; the whole is allowed to remain for a considerable time, and the precipitated sulphate of baryta is collected, heated to redness and weighed. Should the precipitate be reddish from admixture of ferric oxide, it must, in order to obtain accurate results, be fused with carbonate of soda, and the sulphuric acid determined in the aqueous extract from the fused mass (Vol. I. p. 303, b. *a*).

The filtrate from the sulphate of baryta is precipitated by ammonia and carbonate of ammonia, filtered, evaporated to dryness, and gently ignited to remove the salts of ammonia; the residue, after being heated with water and boiled with a little milk of lime, is filtered, precipitated with ammonia and carbonate of ammonia, filtered again, evaporated, and gently ignited; after a little water has been added, it is precipitated once more with ammonia and carbonate of ammonia, evaporated, heated, and the now pure alkali chlorides weighed, and the *potassium* and *sodium* separated by means of chloride of platinum (Vol. I. p. 407, 1 *a*).

In the case of soils which abound in humus, this process does not answer, as the large quantity of organic matter in solution, which is but incompletely destroyed by evaporation with aqua regia, interferes with the precipitation of the hydrates and also the phosphates of sesquioxide of iron and alumina. It is true that the organic matter may be got rid of by evaporation and ignition, but then the ferric oxide and alumina pass into the very unsatisfactory condition of difficultly soluble basic salts. Under such circumstances, the following method is preferable:

1. 300 c.c. of the hydrochloric acid solution serve for the estimation

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* As regards other essentially different methods of estimating phosphoric acid, see TH. SCHLÖSING (Zeitschr. f. anal. Chem. 7, 473 and 8, 500); W. SCHÜTZE (*ibid.* 9, 413).

of the sulphuric acid and alkalies; any substantial variation from the method described in *c*, is unnecessary.

2. 600 c.c. of the above solution is evaporated nearly to dryness in a platinum dish, and pure potash solution is then added in large excess. The whole is evaporated to dryness with the addition of a little carbonate of soda and nitre, ignited so as to destroy the organic matter, macerated with water, and the solution poured off into a flask; the insoluble portion is then transferred to a glass or porcelain vessel, warmed with hydrochloric acid until dissolved, the two solutions mixed, and the mixture made up to 600 c.c. In 300 c.c. of this, the constituents mentioned in *a* are determined, and in the other 300 c.c. the phosphoric acid in the manner already described.

5. Examination of that portion of the Earth which is insoluble in cold Hydrochloric Acid.*

§ 299.

The residue left on treatment of the fine earth with hydrochloric acid, after being dried on the water-bath, weighed, powdered and intimately mixed, is put into a basin, mixed quickly once more, and then portions of 5, 10, and 15 grams are severally weighed off without delay. The portions are best taken from the bulk with a teaspoon. It must not be forgotten, that a powder like the present is very apt to lose its uniformity by shaking, as the coarser particles tend to separate from the finer.

a. The 5 gram portion is ignited with access of air, and the residue weighed. Calculating from the part to the whole, the *total quantity of the anhydrous mineral constituents of the soil which are insoluble in hydrochloric acid* are ascertained.

b. The 10 gram portion is extracted several times by boiling it with a concentrated solution of carbonate of soda, and the *silicic acid* in the filtrate is determined as in this vol. p. 260, *b*. The silicic acid here found may be either that which has been separated in the hydrated condition from decomposable silicates on treating the earth with hydrochloric acid, or it may have been mixed with the clay of the soil as hydrate (this vol. p. 269, *g*).

c. The 15 gram portion is treated in a weighed platinum dish, with about 40 c.c. of pure concentrated sulphuric acid to which a little water has been added, and heated for 10 to 12 hours, so that the excess of acid is nearly but not quite driven off. When cold, it is moistened with concentrated hydrochloric acid, which is allowed to act for some time at a gentle heat; water is then added, and the whole heated and poured through a filter, the operation being repeated until the insoluble residue is thoroughly washed. The filter is spread out on a glass plate, the adherent portion of the residue rinsed into the dish containing the bulk, the whole evaporated, dried at 100°, weighed so as to ascertain the relation in weight to that of the portion of earth insoluble in hydrochloric acid, and thereby also to the weighed fine soil, and then uniformly mixed. The filtrate from the residue is united with the washings in a 500 c.c. measuring flask, mixed, and any silicic acid which may have passed into solution together with the *alumina*, *ferric oxide*, *lime* and *magnesia* are estimated in one 250 c.c. as in 4 *a*, whilst the *potassa* and *soda* are determined in the other 250 c.c. as in 4 *c*. In this connection it must be noted that the copious precipitate of sulphate of baryta obtained on precipitating the sulphuric acid with chloride of barium must be heated to redness after washing and drying, then extracted by boiling with dilute hydrochloric acid, and finally with water, so as not to lose the alkali salts carried down along with it; the solution thus obtained is united with that filtered from the sulphate of baryta.

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* This contains, of inorganic substances, particularly the silicic acid from the silicates decomposable by hydrochloric acid, the silicates not decomposable by hydrochloric acid, and sometimes also fragments of rock; at others, clay together with the hydrated silicic acid often admixed therewith, and quartz sand.

6. Examination of the Residue insoluble in Sulphuric Acid.*

§ 300.

a. From 3 to 4 grams of the residue is boiled repeatedly with a solution of carbonate of soda and the *silicic acid* passing into solution is determined (this vol. p. 269, *g*). The amount thus found, after deducting that in 5 *b*. belongs to the clay in the soil; it is the chief ingredient, after the clayey constituents of the soil, which resists the solvent action of hydrochloric acid but is decomposed by sulphuric acid.

The residue left after boiling with carbonate of soda is washed, dried, heated to redness, and weighed. After calculating the part to the whole, this indicates the sum of the soil constituents which are insoluble in hydrochloric acid and undecomposable by sulphuric acid.

b. From 4 to 6 grams of the residue insoluble in sulphuric acid is ground as fine as possible in an agate mortar, and the powder uniformly mixed; about 3 grams of this is decomposed by hydrofluoric acid (Vol. I. pp. 350 and 351) and the *bases* in it estimated. If *silicic acid* has to be determined directly, and not merely by difference, about 0·5 gram of the fine powder is treated as in Vol. I. p. 348, *b*. *a*. If the total silicic acid thus obtained is deducted from the amount found in 6 *a*, this gives the quantity of silicic acid in the silicates undecomposable by sulphuric acid and present as quartz sand.

c. As by *b*. only the sum of the silicic acid present in quartz and that in combination with bases is obtained, the quartz must be determined directly if it is desired to know how much is in combination; for this purpose, the remaining fine powder from 6 *b*. is employed. The methods suitable for the isolation of quartz (heating with phosphoric acid, heating with sulphuric acid in sealed glass tubes †) have already been described in connection with the analysis of clay (this vol. p. 269).

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* The clay is decomposed by the treatment with sulphuric acid, the bases contained therein passing into solution. The residue thus contains: the silicic acid of the silicates decomposed by hydrochloric acid, that previously existing as hydrate admixed with the clay, and that which was in combination with bases in the clay; further, the silicates undecomposed by hydrochloric and sulphuric acids (fragments of rock), also quartz sand.

† With reference to this method, compare J. HAZARD (Zeitschr. f. anal. Chem. 23, 158), by whom it is shown that in this way a great part, but not by any means the whole, of the silicates is decomposed.

7. Estimation of the Carbon contained in Organic Combination.

§ 301.

Carbon is present in the soil not only in the form of carbonic acid but also as organic substances, and, indeed, chiefly in those which, by mouldering and decay, have been converted into humus (ulmin, humin, and ulmic, humic, geic acids, &c.). It may be deemed sufficient merely to determine the total amount of carbon present in the form of organic matter, or supplementary determinations may be made of the portion soluble in a solution of carbonate of soda (humus acids), of the portion which dissolves on boiling with solution of potash (ulmin, humin), and lastly of the waxy and resinous substances which occasionally occur.

a. Estimation of the total amount of carbon contained in organic combination.

This can be effected:

α. By ultimate Analysis in the Dry Way.

aa. If the fine soil dried at 125° is analysed as in this vol. p. 72, § 191, then from the carbonic acid thus obtained must be deducted that existing as carbonates (§ 303, *a*). As the amount of the carbon in the organic matter is thus found from the difference between the two estimations, the accuracy of the result is affected.

bb. R. Warington and W. A. Peake * recommend that in the first place the carbonates present should be decomposed, and for this purpose the finely powdered soil (about 10 grams) is covered with a concentrated solution of sulphurous acid and the whole evaporated to dryness. The residue is then put into a platinum boat and the organic matter burnt off in a combustion-tube by the aid of a current of oxygen in the presence of oxide of copper (see this vol. p. 25, § 178). Warington and Peake employ as a receiver for absorbing the oxides of nitrogen and water vapour, a wash-bottle containing concentrated sulphuric acid, and a U-tube filled with pumice, moistened with sulphuric acid, collecting the carbonic acid in two U-tubes, filled with caustic soda (or soda lime).

cc. G. Loges † recommends weighing out the fine soil to be examined, in a very thin glass dish (a Hoffmeister basin), then to add dilute phosphoric acid (with sandy soil there should not be any great excess of the acid), and evaporate to dryness on the water-bath. The dish and its contents are ground up, mixed with powdered oxide of copper and placed in a combustion-tube about 60 cm. long, open at both ends, and containing in the fore part a layer of granulated oxide of copper about 20 cm. long between asbestos plugs. The combustion-tube is connected at the farther end with two wash-bottles, the first containing potash solution, the other baryta water, and in front, first with a drying cylinder, filled in the upper half with cotton wool, then with an absorption-tube for containing baryta water, next with a wash-bottle containing baryta water, and finally with an aspirator. The drying cylinder containing cotton-wool is for the purpose of retaining any oxygen compounds of nitrogen, together with water; a copper spiral in the fore part of the tube may, however, be used instead. The baryta water bottle interposed between the absorption-tube and the aspirator is for ascertaining whether the whole of the carbonic acid has been retained by the former, as it must be to obtain successful results.

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* Ber. der deutsch. chem. Ges. 13, 2096.

† Landwirthschaftl. Versuchsstationen, 28, 229, and 241; Zeitschr. f. anal. Chem. 22, 619.

The granular oxide of copper is first heated to bright redness, air being drawn through the apparatus meanwhile; 100 to 150 c.c. of baryta water—titrated by the aid of a solution of oxalic acid containing 10 grams per litre—is then introduced into the absorption-tube, and the combustion-tube is slowly heated, beginning at the fore part and continuing backwards, a fairly rapid stream of air (kept constant by means of a MARIOTTE's bottle) being drawn through the apparatus meanwhile. Finally, the hydrated oxide of barium remaining in 25 or 50 c.c. of the clear baryta water is determined by oxalic acid, using rosolate of potassa as indicator; this gives the amount of baryta precipitated by carbonic acid, and consequently the carbonic acid and the carbon.*

β. *By Oxidation in the Wet Way, with Chromic Acid and Sulphuric Acid in the manner described in this vol. p. 323, bb.*

This method, formerly much used, is referred to here merely in order to point out that it is not applicable to soil analysis. According to WARINGTON and PEAKE (*loc. cit.*) only 80 to 90 per cent. of the carbon is estimated in this way, and according to G. LOGES (*loc. cit.*) only 64 to 96 per cent.; the investigations of the latter in fact show that many of the organic substances in soils, on oxidation, yield acetic acid, and this resists further oxidation by chromic acid.†

According to F. SCHULTZE, every 58 parts of carbon represent, on the average, 100 parts of organic matter in soil, and every 60 parts of carbon 100 parts of humus.

b. Estimation of Humus.

The brown or black products, resulting from the action of air and moisture on the residual matter of plants in the soil, which greatly affect its nature and fertility, although opinions differ as to their mode of action, are styled humus substances. Attempts have been made to isolate and characterise these as individual chemical compounds, under various names—Ulmic acid, humic acid, ulmin, humin, &c. Notwithstanding these numerous investigations,‡ it cannot be said that the subject is exhausted or that any definite result has been obtained, and this is easily understood from the fact that the principal humic constituents are very much alike in their properties, and that neither they nor their compounds can be obtained crystallised. Certain facts, however, have been established, and, being of importance in judging of the nature of soils, must be considered here. To these belong the fact that many of the humic constituents (the humus acids) dissolve in boiling solutions of alkali carbonates—whether owing to the humus acids being in a free state, or whether their saline compounds are decomposed by alkali carbonates—whilst other humic substances are not so dissolved, although they dissolve in caustic alkalies, being of course thereby converted into humus acids.

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* Compare the estimation of carbonic acid in atmospheric air (§ 336 to § 340).

† Compare CROSS and BEVAN, Zeitschr. f. anal. Chem. 26, part 1.

‡ See the collection of many old investigations in L. GMELIN's, "Handbuch der Chemie," 4th edn. by K. KRAUT, 7, 1855; OTTO in SPRENGEL's "Bodenkunde," p. 430; FR. SCHULZE, Journ. f. prakt. Chemie, 47, 241; W. DETMER, "Landwirthschaftliche Versuchsstat. 14, 248; GRANDEAU's "Handbuch," pp. 108 and 112; O. PITSCH, "Landwirthschaftliche Versuchsstat." 26, 1.

a. Estimation of the Humus Matters soluble in Carbonates of the Alkalies (Humus Acids).

From 10 to 100 grams of the air-dried earth (according as the qualitative analysis has shown the presence of a larger or smaller quantity of the acids of humus) is digested for about 4 hours on the water-bath with a solution of carbonate of soda (1 part of the anhydrous salt to 10 parts of water), then filtered, and washed with boiling water. The paler or darker brown filtrate can either be treated by the method described in this vol. p. 519 (acidification with acetic acid, boiling, precipitation with acetate of lead, &c.), or it may be acidified with hydrochloric acid, the brown flocks collected on a weighed filter which has been previously dried at 100°, washed with cold water until the filtrate is no longer acid, dried at 100°, and weighed. It is then incinerated, the weight of the ash deducted from the weight first obtained, and the difference set down as acids of humus. As in the latter process the filtrate is always coloured, the first method is preferable when the solution is pale brown.

β. Estimation of the Humus Matter insoluble in Carbonates of the Alkalies (Humin, &c.).

The residue left in *a*, after being digested on the water-bath in a porcelain dish for some hours with a solution of 1 part of potash in 10 of water, replacing the water as it evaporates, is diluted, and the liquid decanted through a filter; the residue is then again treated with potash solution in a similar manner, diluted, filtered, washed, and the humus acids produced from the humin estimated in the filtrate as in *a*.*

c. Estimation of Waxy and Resinous Substances.

If these substances, which are only found in appreciable quantities in some kinds of soil, have to be estimated, a quantity of the earth corresponding with 100 grams of the fine earth dried at 125°, is dried in the water-bath, boiled repeatedly with strong alcohol, the filtrates collected in a flask, the spirit distilled down to half, and the residue allowed to cool, which will cause the wax present to separate; this is collected on a weighed filter, washed with cold spirit of wine, and its weight determined. The filtrate from this is evaporated, finally with the addition of water, until the alcohol is entirely removed, and the resin which separates is washed with water, dried and weighed. (If the total quantity of wax and resin is in any way considerable, it must be deducted from the weight of the humus acids, as the waxy and resinous matters have been weighed along with the latter.)

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* Fr. Schulze has proposed to determine the humic substances extractable by alkali solutions, with permanganate of potassa, in the same way as is used for organic matter dissolved in water (see this vol. p. 125). For the performance of this supplementary estimation, Schulze boils 5 grams of "fine soil" with 100 c.c. of water, and a solution of potassa of 0·1 to 1·0 per cent. strength (E. Wolff used 0·5 per cent.), according to the amount of humus in the soil; the mixture is poured on to a filter—instead of using a paper filter the lower part of the funnel is filled with ignited, fine-grained sand—washed, and made up to 150 or 200 c.c. A few c.c. of this solution is employed for the above-named estimation, which naturally cannot give a very accurate result.

8. Determination of the Nitrogenous Constituents of the Soil.

§ 302.

Nitrogen may be present in the soil in three different states of combination, namely, as nitric acid (or nitrous acid), as ammonia, and in organic compounds. In order to know the character of a soil, it will not suffice to determine the total amount of the element, we must also know the form in which it occurs.

a. Estimation of Nitric Acid.

As salts of nitric (and also of nitrous) acid are not retained on extracting the soil with water, all the nitrates (and nitrites) present in it will be found in the aqueous extract, in which they have already been determined, see § 297, *c*.

b. Estimation of Ammonia.

As the soil contains ammonia compounds in such a form that they are not completely removed in the aqueous extract, the amount of ammonia found in the latter, even if it can be estimated, affords no indication of the total quantity existing in the soil; a separate estimation must therefore be carried out in order to determine it. According to the investigations of Knop and W. Wolf,* as well as those of A. Baumann,† ammonia compounds are present in very small quantities only in soils, at most 2 to 3 parts of ammonia per 100,000 of soil. The following methods of estimation have been recommended:

α. Schlösing's *Process* (Vol. I. p. 179, *b*).

E. Wolff ‡ advises the employment of 50 grams of the air-dried fine soil, moistened uniformly with 40 c.c. of *cold*, *fully concentrated* caustic soda. The ammonia will be all driven out after the lapse of 48 hours. As, however, ammonia is continuously evolved by caustic soda from soils containing humus, even when these are free from ammonia compounds, this method is inapplicable to such soils. §

β. Distillation with Water and Calcined Magnesia (Vol. I. p. 178, 3 *a*).

E. Wolff (*loc. cit.*) proposes distilling 100 grams of air-dried fine soil with 500 c.c. of water and 5 grams of freshly calcined magnesia. Grandeau ‖ remarks hereon that the process, if carried out in this way, cannot yield accurate results, as, after the ammonia which is present has been driven off, other nitrogenous constituents of the soil will also evolve ammonia. Very accurate results can be obtained, according to him, by the following method, also due to SCHLÖSING, in which the ammonia is not determined by direct distillation of the soil, but from the hydrochloric extract.

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* Chem. Centralblatt. 1860, 540.

† Landwirthschaftl. Versuchsstat. 1886, p. 284.

‡ His "Anleitung zur chem. Untersuchg. landwirthschaftl. wichtiger Stoffe," 3rd edn. p. 47.

§ See also earlier opinions, particularly A. Baumann (landwirthschaftl. Versuchsstat. 1886, p. 255). Whether better results are obtainable by milk of lime still remains to be investigated.

‖ His "Handbuch," German Edition, p. 116.

The method is carried out as follows :

aa. One vol. of hydrochloric acid is mixed with four vols. of water, and any ammonia which may possibly be present is determined in the diluted acid, per c.c.

bb. A quantity of air-dried fine soil, corresponding with 100 grams of the soil dried at 125°, is placed in a 1- to 2-litre flask, 50 c.c. of the dilute acid *aa.* is added without warming, followed by another 50 c.c. after the carbonic acid is evolved, and a further quantity if necessary until the hydrochloric acid is unmistakably in excess, even after repeated shaking. Water free from ammonia is now added, so that the total amount of liquid is about 400 c.c. ; the whole is mixed uniformly, and the flask weighed and allowed to stand until the liquid over the sediment is clear ; it is then drawn off carefully by means of a pinch-cock syphon, and the weight of the decanted liquid is ascertained by reweighing the flask. In order to ascertain what proportion of the whole liquid has been removed, the undissolved residue is collected, washed, dried at 125°, and its weight deducted from the original weight of the total contents of the flask. The ammonia in the decanted solution is now determined, calculated to the whole solution, and then to 100 grams of fine soil dried at 125°.

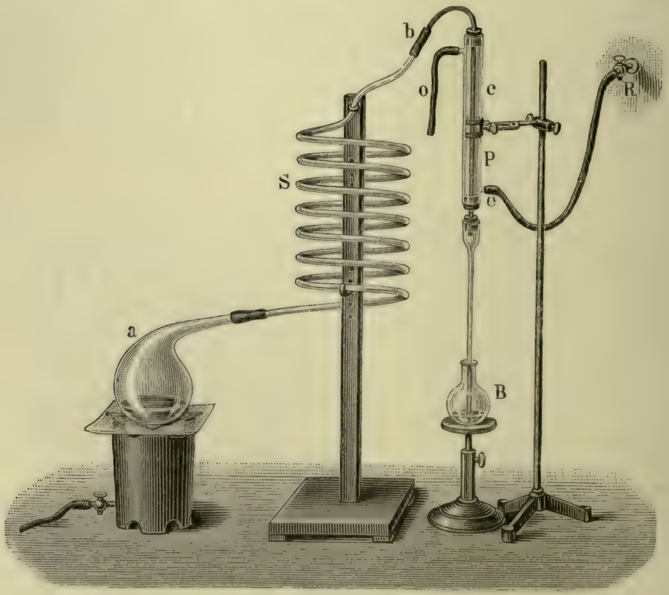

Fig. 126.

For the estimation of the ammonia in the hydrochloric solution, the apparatus in Fig. 126 is employed, which differs from that usually used for distilling ammonia, in that the possibility of impurities from the constituents of the glass occurring in the ammoniacal solution to be titrated is excluded, and that the whole of the ammonia is obtained in a very small bulk of liquid. The hydrochloric acid solution of the soil is put into the retort *a*, adding freshly calcined magnesia so that the latter may be decidedly in excess. The condensing tube S is connected on the one hand with the flask *a*, and on the other at *b* with the bent platinum tube *c*, which passes through a small condenser *P* fed from the reservoir *R*. The lower extremity of the platinum tube *c* dips, at *e*, into a funnel-shaped glass tube extending down into an accurately measured quantity of very dilute, titrated sulphuric acid containing about 0·001 gram of SO_3 per 1 c.c., which has been placed in the flask *B*. When the contents of the flask *a* have been heated until it is certain that all the ammonia has passed over into *B*, the excess of acid is titrated by lime water which has been previously standardised to the acid, using tincture of litmus* as indicator. A. Baumann† advises, particularly when glass condensing tubes are used, that the ammonia in the distillate should be determined azotimetrically.

γ. *The Azotimetric Method.*

This simple method for estimating ammonia, which yields very accurate results, was originally proposed by W. Knop,‡ and is recommended by him and W. Wolf§ for the estimation of ammonia in soils. The process has subsequently been repeatedly examined, modified, and improved, particularly by E. Dietrich,‖ W. Knop,¶ P. Wagner,** and F. Soxhlet.†† It is based upon the known action of an excess of alkali hypobromite on ammonia salts, which results in all the nitrogen of the ammonia being liberated as such; the method can, however, only be used for the determination of ammonia in soils or their hydrochloric solutions (Dietrich, A. Baumann) provided they contain no other nitrogenous compounds decomposable by alkali hypobromites with evolution of nitrogen, urea, for example, and are not rich in humus. Thus in the case of freshly manured soil, or humous soils, such as peaty soil, the method would give very inaccurate results.‡‡ As the azotimetric process for estimating ammonia plays a much more important part in the analysis of manures than in that of soils, it will be described under that head in Appendix V. of the Special Division (§ 322).

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* To attain the highest degree of sensitiveness, Schlösing recommends the following mode of preparation: A highly concentrated solution of litmus in distilled water is boiled with a little hydrate of lime, allowed to settle, decanted, filtered, and mixed with 5 or 6 times its volume of alcohol; the blue precipitate thus produced is collected, and after being washed a few times with weak spirit of wine, is preserved under alcohol in a closed bottle. To prepare the litmus tincture, a little of the blue precipitate is suspended in water, then just supersaturated with dilute sulphuric acid, the precipitated sulphate of lime filtered off, the filtrate boiled once to drive off the carbonic acid, and then exactly neutralised with potash or soda.

† Landwirthschaftl. Versuchsstat. 1886, p. 255.

‡ Chem. Centralbl. 1860, 244.

§ *Ibid.* 1860, 257.

‖ Zeitschr. f. anal. Chem. 5, 36.

¶ *Ibid.* 9, 225; 14, 248; 25, 301; and 26, Part I.

** *Ibid.* 13, 383 and 15, 250.

†† *Ibid.* 16, 81.

‡‡ See W. Knop (Zeitschr. f. anal. Chem. 9, 225); Hüfner (*Ibid.* 10, 486); Pagel (*Ibid.* 15, 282); A. Morgen (*Ibid.* 20, 37); E. Schulze (*Ibid.* 21, 1); A. Baumann (Landwirthschaftl. Versuchsstat. 1886, 281).

c. Estimation of the Nitrogen contained in Organic Compounds.

a. The total nitrogen is determined by igniting an air-dried sample of soil with soda lime (this vol. pp. 49–55), and deducting therefrom the nitrogen present as nitric acid and ammonia. If the soil contains only a small portion of organic matter, 0·3 to 0·5 gram of pure cane-sugar has to be mixed with the sample in order to obtain all the nitrogen of the nitric acid as ammonia. In order to ensure thorough admixture, E. Wolff recommends stirring the sample up with the aqueous solution of sugar and then drying it; E. Schulze (comp. this vol. p. 50) has shown that, under these circumstances, small quantities of nitric acid are completely converted into ammonia.

β. The sum of the nitrogen present in organic matter and as ammonia is determined by the Kjeldahl process, referred to in Appendix V. "Analysis of Manures," after having driven off any nitric acid which may be present by evaporating it with dilute sulphuric acid. By deducting from the amount of ammonia thus obtained, that present in the soil as such, that corresponding with the nitrogen of the organic matter is obtained (see also § 329, *γ*).

9. Supplementary Estimations

§ 303.

a. Estimation of Carbonic Acid.

The carbonic acid is determined according to one of the methods described in Vol. I. pp. 337–346, in a sample of the air-dried fine soil, which should be larger or smaller in proportion to the amount of the carbonic acid, any absorbed carbonic acid having been previously removed from the sample by boiling it with water.

b. Estimation of the unoxidised Sulphur.

Soils frequently contain small quantities of unoxidised sulphur, for the most part in the form of sulphides (pyrites). This can generally be easily detected by determining the sulphuric acid in the unignited soil, and then repeating the determination on an ignited portion; the latter result will generally be higher than the first (E. Wolff). To estimate the unoxidised sulphur, 50 grams of the air-dried fine earth, in a platinum dish, is moistened with a concentrated solution of pure nitre, some pure carbonate of soda is added, and the whole dried, and heated gradually to redness, when the mass smoulders and the organic matter is completely oxidised. When cold it is softened with water, heated in a porcelain dish with hydrochloric acid and a little nitric acid, filtered, the silicic acid separated, and the sulphuric acid determined; from the result, the amount found in § 298 *c* is deducted, the difference representing the quantity of unoxidised sulphur in the soil.

c. Reaction of the Soil.

Finally the reaction of the soil should be noted. To ascertain this, a moderately moist lump of the fresh soil is placed on sensitive litmus paper; if the reaction is acid, it should be noted whether the red spots on the blue paper lose their colour or are permanent; the former is the case if the acidity is due to free carbonic acid only.

d. Further Estimations.

In certain circumstances it may be advisable to extend the examination still further, for example, to the estimation of the hydrated ferric oxide and the hydrate of alumina, A. Müller,[*] W. Knop;[†] to the quantity and nature of the gases absorbed by the soil, Blumtritt,[‡] Reichardt;[§] the behaviour of the moistened soil, or the soil saturated by caustic potassa solution towards oxygen or air, W. Wolf, Fr. Schulze;[||] to the substances passing into ammoniacal solution along with the humus, in Schlösing's (§ 295) method of humus determination (Analysis of the "Matière noire");[¶] or to the behaviour of the soil in the dialyser, Petermann,[**] Sestini.[††] On these points, however, the reader is referred to the original treatises.

10. Statement of the Results.

§ 304.

The results of the chemical examination require judicious arrangement in order to give a clear representation of the composition of the earth. The plan on p. 536 seems to be best suited for the purpose; the numbers are arbitrary, and are only given to illustrate the principles of arrangement.

V. ANALYSIS OF MANURES.

A. General.

§ 305.

By manures is to be understood, first, such as are produced in agriculture, and consisting chiefly of urine, animal excrement, and litter, that is, *stable manure;* and secondly, such as are purchased by the farmer: *artificial manures.* The number and varieties of the latter have, in course of time, greatly increased owing to the joint action of agriculture, trade, and technical industry in endeavouring to procure from widely different sources and in manifold combinations and mixtures, the substances needed for plant food, especially phosphoric acid, potash and nitrogen, in the form required for the various purposes of agriculture and vine-growing.

Whilst, as a rule, the chemical examination of stable manure possesses a greater scientific interest, yet the analysis of commercial manures is of very great practical importance, as their widely varying values must be determined by chemical analysis, which reveals the content and mode of combination of their effective constituents.

As manure manufacturers and dealers now guarantee certain percentage compositions, and the farmer is in a position to prove by the aid of the agricultural experimental stations and commercial labora-

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[*] Landwirthschaftl. Versuchsstat. 4, 226; also Journ. f. prakt. Chem. 98, 4.

[†] Landwirthschaftl. Versuchsstat. 8, 41.

[‡] Journ. f. prakt. Chem. 98, 418.

[§] *Ibid.* 98, 458; also Zeitschr. f. anal. Chem. 7, 185.

[||] E. Wolff's "Anleitung z. chem. Untersuchg. landw. wicht. Stoffe," 3rd edn. pp. 41 and 42.

[¶] Grandeau's "Handbuch," p. 113.

[**] Landwirthsch. Versuchsst. 15, 468.

[††] *Ibid.* 29, 459.

100 *Parts of Fine Soil dried at* 125° *contain :*

		Soluble in water.	Compounds decomposed by hydrochloric acid.	Compounds decomposed by sulphuric acid.	Compounds not decomposed by hydrochloric or sulphuric acids.	Total.
Substances which withstand heating.	Potassium	0·005	0·150	0·200	1·500	1·855
	Sodium	0·004	0·050	0·100	1·000	1·154
	Lime	0·009	0·500	0·150	0·200	0·859
	Magnesia	0·002	0·400	0·100	0·150	0·652
	Alumina	—	2·500	3·000	4·000	9·500
	Ferrous oxide	—	0·100	—	—	0·100
	Ferric oxide	—	2·000	1·000	0·300	3·300
	Mangano-manganic oxide	—	0·060	—	—	0·060
	Sulphuric acid	0·008	0·020	—	—	0·028
	Phosphoric acid	0·001	0·080	0·020	—	0·101
	Carbonic acid	—	0·600	—	—	0 600
	Chlorine	0·002	—	—	—	0·002
	Silica in combination	0·007	4·000	6·000	12·000	22·007
	Silica as quartz	—	—	—	55·106	55·106
	Total	0·038	10·460	10·570	74·256	**95·324**
		Nitrogen.	Carbon.	Hydrogen.	Oxygen.	
Combustible or decomposable at a red heat, or volatile matter.	Ammonia	0·0025	—	0·0005	—	0·003
	Nitric acid	0·036	—	—	0·140	0·140
	Humic acid	—	1·200	0·800		2·000
	Humin	—	0·200	0·133		0·333
	Other organic substances	0·050	0·580	0·370		1·000
	Chemically combined water	—	—	1·200		1·200
	Total	0·0885	1·980	2·6075		**4·676**
						100·000

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tories, whether the manures are up to guarantee, the analysis of manure is a very important subject in many chemical laboratories. On this account, many chemists have occupied themselves with the task of finding out the most suitable methods for examining them, especially from different points of view. Whilst with some, the chief object has been the accuracy of results, others have striven after the most speedy and simplest possible methods; and repeatedly agreements have been made between the experimental stations and the manufacturers to regulate the methods of analysis with a view to attain uniform results.

In the following, an endeavour will be made to take into account these different points of view as far as possible, and the most efficient way of arranging the whole Section will be to pass gradually from the simpler to the more complicated, commencing first with manures whose value is due to a *single* constituent and then proceeding to those in which *two or more* of the component parts require to be estimated. In the first place, however, attention must be directed to the manner of taking samples, as the most accurate analysis is valueless if the sample does not accurately represent the average composition of the bulk.

B. Sampling.*

§ 306.

In taking samples, the following precautions should be adopted:

1. If a number of lumps are present, as, for example, in phosphorite, a true sample can only be taken after breaking down a large quantity and carefully mixing the mass thus obtained.

2. If the bulk from which the sample is to be drawn consists of fine powder together with lumps or coarse pieces, these should be separated by sifting, and the lumps or pieces ground down or cut up, and mixed uniformly with the sifted portion.

3. If the material of which samples have to be taken is more or less powdery, and stored in barrels or sacks, it is not sufficient to take portions from the upper parts and mix them together, because the layers in the casks or sacks may differ. As the regular mixing of the contents of a number of barrels or sacks is attended with considerable difficulty, a *sampling tool* † is generally used in such cases, consisting of a hollow cylinder, with a point *b* and a handle *a*, as shown in Fig. 127. This, which is of stout sheet-iron 60 cm. long and 3 cm. in diameter, is pushed into the barrel or sack and turned once round, when it becomes filled with the material; it is then drawn out slowly, and the contents emptied, the process being repeated as often as appears necessary to obtain an average sample, and in any case until at least from 1 to

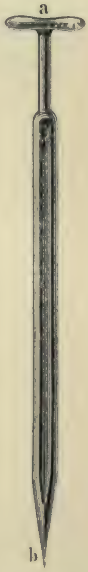

Fig. 127.

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* With respect to the influence of the method of sampling manures on the results of the analysis, Barral and Duval carried on an extensive investigation with guano (Zeitschr. f. anal. Chem. 15, 490).

† E. Schumann, "Anleit. zur Untersuchung. der kaüflichen Düngemittel," &c., 1876; P. Wagner, "Lehrbuch der Düngerfabrikation." Brunswick: F. Vieweg & Son, 1877, p. 176.

2 kilograms of the material have been taken out. For many manures, a sampler, with a knife edge at the end instead of a point, is preferable.

4. If it is required to take a small sample, for sending away or for further preparation, from a relatively large quantity of more or less powdery substance, the bulk is mixed uniformly on a suitable surface (on a table, a cloth placed on the floor, or in some such way); it is then spread out into a thin circular layer of uniform thickness and one or two segments are taken, so that the weight of the sample is about 500 grams.

5. The samples intended for analysis should be packed or stored in tightly stoppered glass bottles, or in the case of manures which are not acid, in tin boxes with tightly fitting lids.

6. In the laboratory, the sample must as a rule be again broken down. If a determination of the moisture has to be made as well as an analysis of the dried sample, for the first a large sample should be taken either as it is, or after rapid mixing in a large mortar, according to circumstances. The material is then passed, either as it is or after drying somewhat, through a sieve of 1 to 1·5 mm. mesh, and the coarser parts are ground so that the whole can be passed through the sieve, and mixed uniformly. A small sample is now taken by a spoon, ground fine, dried at the temperature at which the moisture was determined, and used for analysis. If no moisture determination has to be made, and the material has to be examined in the state in which it is, a sample, as uniform as possible, must be quickly prepared, avoiding any circumstances favouring a change in its hydroscopic state; it is then always advisable to dissolve a large weighed sample, and employ aliquot parts of the solution for the estimations.

7. Wet samples may under certain circumstances be uniformly mixed and prepared for analysis, at any rate for the determination of certain of the constituents, by mixing a large weighed quantity of the manure with a weighed amount of freshly burnt gypsum. If the correct proportions are taken, a mixture is obtained which can be ground, sifted and uniformly mixed. Should loss of ammonia be feared the gypsum must, previously be ground up with 3 to 5 per cent. of concentrated sulphuric acid. It is scarcely necessary to say that, when gypsum is used for mixing, its weight must be taken into consideration when measuring out portions of the substance for analysis.

C. Analysis of Manures the value of which is solely or almost exclusively due to the Phosphoric Acid they contain.

I. THOSE IN WHICH THE WHOLE OF THE PHOSPHORIC ACID IS PRESENT IN COMPOUNDS INSOLUBLE IN WATER.

§ 307.

To this category belong ignited bone phosphates (bone ash, bone black), precipitated phosphate of lime (basic slag or Thomas slag), mineral phosphates (apatite, phosphorite, coprolites, osteolites, Navassa-, Sombrero-, Carolina-phosphate, &c.), and many kinds of guano (Baker guano, Maracaibo guano, Jarvis guano, &c.). All these phosphates contain tribasic phosphoric acid only (orthophosphoric acid), chiefly combined with lime, mostly indeed as basic orthophosphate of lime, tricalcium phosphate, $3CaO,PO_5$; many, however, such as the cakes or clinkers of the Baker- and Jarvis-guano,* and occasionally the precipitated phosphate of lime, contain so-called neutral orthophosphate of lime, dicalcium phosphate, $2CaO,HO,PO_5$. In the former this orthophosphate remains unchanged on ignition, but in the latter it becomes converted into pyrophosphate, $2CaO,PO_5$.

1. Determination of the Moisture.

From 3 to 5 grams are dried until the weight is constant. As regards the temperature, 100° is the most convenient, and is on that account frequently used, although drying at 110° is more effective, and therefore to be preferred as a rule. In the case of bone black, such a high temperature is necessary. Weighing and drying are conveniently effected in a light weighing-tube with hollow stopper, Fig. 128.

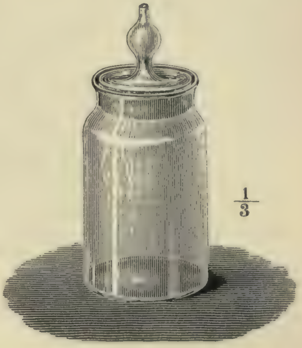

Fig. 128.

2. Estimation of the Phosphoric Acid.

Of the numerous possible methods for estimating the phosphoric acid, the gravimetric *molybdenum process* has proved to be the most trustworthy under all circumstances for the phosphates now under consideration.† In addition to this, the method published by C. Glaser ‡ is also described.

a. Dissolving the Substance.

§ 308.

α. If the phosphate to be examined is quite or almost free from organic matter, readily soluble in acid, and free or nearly free from easily decomposable silicates, as, for example, precipitated phosphate of lime, moreover, if it is in a fine and uniform powder, 0·4 or 0·5 gram is dissolved in warm dilute nitric acid, diluted somewhat, and filtered. If, on the other hand, the substance is not finely divided and not quite uniform, 4 to 5 grams are dissolved in the prescribed manner, and made up to 500 c.c., or 8 to 10 grams to 1000 c.c., 50 c.c. of the solution being employed.

β. If the substance to be examined is free or almost free from organic matter, less easily soluble in acids, or richer in decomposable silicates, such as phosphorite or basic slag, then 0·4 to 0·5 gram is digested with 8 c.c. of fuming hydrochloric acid for an hour on the water-bath, the solution evaporated to dryness at 100°, and the residue moistened with 5 c.c. of hydrochloric acid; a little water is then added and the solution filtered from the insoluble residue of sand and silica, which is usually slight in the case of phosphorite, but considerable from basic slag. The solution is evaporated again almost to dryness, 10 c.c. of nitric acid of sp. gr. 1·2 is added, the mixture evaporated nearly to dryness, 10 c.c. more nitric acid added, the liquid evaporated once more almost to dryness, and finally 5 c.c. of nitric acid and a little water is added and the whole transferred to a beaker. If the substance is not in fine powder or homogeneous, in this case also it is advisable to prepare 500 or 1000 c.c. of solution, dissolving from 4 to 5 or 8 to 10 grams of substance respectively, in the manner already described, and then to use 50 c.c. for the analysis. If the residue insoluble in hydrochloric acid is considerable, it is necessary as a precaution to submit it to the treatment described in γ, uniting the nitric acid solution thus obtained with the main solution, or to examine it independently for phosphoric acid.

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* C. Gilbert, Zeitschr. f. anal. Chem. 12, 1.

† See Zeitschr. f. analyt. Chem. 21, 289.

‡ See *Ibid.* 24, 178.

γ. Should the substance to be examined be richer in organic matter, or only completely dissolved with difficulty by hydrochloric acid, or should a pyrophosphate have been formed by ignition, 0·4 to 0·5 gram is fused, in a platinum crucible, with 3 to 4 parts of carbonate of soda, and when organic matter is present, 1 part of nitrate of potassa, the fused mass is treated with water, placed in a beaker, diluted, the beaker covered with a watch-glass, and hydrochloric acid added by degrees until it is in considerable excess; the watch-glass is then rinsed, and the solution transferred to a porcelain basin and evaporated to dryness on a water-bath. To the residue, 10 c.c. of hydrochloric acid is added, then a little water, the whole heated, filtered, and the filtrate evaporated almost to dryness; 20 c.c. of nitric acid sp. gr. 1·2 is then added, the solution evaporated almost to dryness, another 20 c.c. of nitric acid is added, again evaporated almost to dryness, and lastly, 5 c.c. of nitric acid is added and the whole transferred to a beaker by the aid of water. In this method it is advisable, even when more trouble is entailed, to commence with the production of a finely powdered and homogeneous substance, as the fusion of a much larger sample, in order to obtain a 500 or 1000 c.c. solution, is attended with considerable difficulty.

δ. In the case of bone black, it is best to first heat about 10 grams with some 50 c.c. of water to boiling, gradually add about 40 c.c. of nitric acid of sp. gr. 1·2, and after the heating has been continued for an hour, dilute, filter into a litre flask and wash until the final washings no longer have an acid reaction. The contents of the filter are then dried and the carbon burnt off. If a residue is left, it is warmed with nitric acid, diluted, filtered into the main solution, made up to 1000 c.c., and 50 c.c. is taken for analysis.

b. The estimation.

*a. Molybdenum Method.**

§ 309.

aa. To the nitric acid solution, about 50 c.c. in volume, obtained by one of the processes given in § 308, corresponding with 0·4 to 0·5 gram of phosphate, and therefore containing 0·1 to 0·2 gram of phosphoric acid, so much molybdenum solution * is added that there are about 50 parts of molybdic acid to 1 part of phosphoric acid, that is, in general, 150 c.c. of the 5 per cent. solution, and the mixture left for 4 to 6 hours at 50°. To a clear sample of the liquid decanted from the precipitate, an equal volume of molybdenum solution is added and the whole warmed at 50° for an hour, in order to test whether the precipitation is complete; should this not be the case, more molybdenum solution must be added to the main solution and again warmed for a few hours. The liquid is now decanted through a small filter and the precipitate (the greater part of which is left in the beaker) washed repeatedly with small quantities of a liquid prepared by mixing 100 parts of the molybdenum solution with 20 parts of nitric acid of sp. gr. 1·2 and 80 parts of water†, until lime is no longer present in the filtrate, and the last drops no longer give a turbidity in strong spirit of wine mixed with a little dilute sulphuric acid.

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* Although the details of the molybdenum method have already been described in Vol. I. p. 307, it is necessary to repeat it here as in the interim appreciable improvements have been effected, see particularly the work of Abesser, Jani, and Märcker (Zeitschr. f. anal. Chem. 12, 239), and Peitzsch, Rohn, and P. Wagner (*ibid.* 19, 444).

The phosphomolybdate of ammonia is now dissolved in as small a quantity as possible of aqueous ammonia. This is most conveniently effected as a rule by allowing slightly warm ammonia ‡ to drop through the filter into the beaker holding part of the precipitate, until the latter is just dissolved. It is then diluted with a little water, filtered through the same filter into a smaller beaker (holding about 200 c.c.) and the beaker and filter washed with dilute ammonia (1 vol. of ammonia to 3 vols. of water). In order to determine more precisely the excess of ammonia, dilute hydrochloric acid is added until the greater part of the ammonia is neutralised (the precipitate formed should partly redissolve on shaking), and then 6 to 8 c.c. of undiluted ammonia is added, which may be conveniently employed to wash out the beaker and the filter again. The liquid in the small beaker, which should not exceed 70 to 75 c.c., is left until *quite cold*, and then 15 to 20 c.c. of chloride of magnesium mixture § is added from a burette or pipette, *drop by drop with constant stirring*, and lastly so much undiluted ammonia that the total present is equal to about one fourth of the liquid, that is, usually about 20 c.c. more; the phosphate of ammonia and magnesia is thus obtained as a distinct crystalline precipitate. After about four hours, it is collected on a filter, the residue in the beaker, together with the portion of the filtrate, is brought on to a filter and washed with a mixture of

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* The molybdenum solution (5 per cent.) is prepared by dissolving 1 part of molybdic acid in 4 parts of 8 per cent. solution of ammonia and pouring it into 15 parts of nitric acid of sp. gr. 1·2. It may also be prepared from molybdate of ammonia by dissolving 150 grams of pure powdered molybdate of ammonia in 1 litre of water at a gentle heat, and pouring the solution into 1 litre of nitric acid of sp. gr. 1·2; if the molybdate of ammonia employed is NH_4O,MoO_3, the solution will contain 5·5 per cent., if $3NH_4O,7MoO_3+4H_2O$, it will contain 6·1 per cent. of molybdic acid. Whichever way the solution may have been prepared, it is left for a few days at a moderate temperature, decanted if necessary, and kept in the dark.

† P. WAGNER dilutes the molybdenum solution for the washing, in the proportion of 1 vol. of molybdenum solution to 3 vols. of water.

‡ MÄRCKER and P. WAGNER both dilute the ammonia with 3 parts water.

§ This, as is explained in Vol. I. p. 307, is in every respect preferable to the sulphate of magnesia mixture. As crystallised chloride of magnesium is now easily procured, the mixture is prepared from 110 grams of crystallised chloride of magnesium, 140 grams of chloride of ammonium, 700 c.c. of ammonia (containing 8 per cent. of NH_3), and 1300 c.c. of water; after a few days the mixture is filtered if necessary (MÄRCKER). For the precipitation of 0·1 gram of phosphoric acid, 10 c.c. of the chloride of magnesium mixture should be used, containing about double the quantity of magnesia necessary to precipitate the phosphoric acid.

1 part of ammonia and 3 parts of water, until the last drops no longer cause a turbidity in acid silver solution; the precipitate is then dried, the filter incinerated, and the precipitate heated to redness, finally 1 to 2 minutes over the blowpipe, and weighed. Care must be taken (*a*), that the filtrate is tested with chloride of magnesium to make sure that all the phosphoric acid is precipitated, and, in analyses where the greatest accuracy in the results is required, (*b*), the pyro-phosphate of magnesia should be warmed with hydrochloric acid to ascertain whether any silica is left, which in that case must be weighed and deducted. The hydrochloric solution, when treated with sulphuretted hydrogen, must not yield any, or at all events no weighable, precipitate of sulphide of molybdenum. If this should happen, the result would be too high.

The molybdenum method has undergone many modifications. Although all these cannot be described, two may be mentioned which are in use in many experimental stations, of which *bb* is calculated to economise time, and *cc* also to effect an economy in the use of the molybdenum solution.

bb. First modification by P. WAGNER* (this differs from *aa* only in some slight alterations in the process): 25 to 50 c.c. of the phosphate solution containing 0·1 to 0·15 of phosphoric acid is placed in a porcelain basin and 100 to 150 c.c. of the molybdenum solution prepared from molybdate of ammonia (see p. 541, note *) is added. The mixture is warmed to about 80° in a water-bath or over a lamp, with frequent stirring, and put aside for an hour. It is then filtered, and the yellow precipitate (which of course need not be wholly rinsed on to the filter) is washed with dilute molybdenum solution (p. 541, note †); the porcelain basin is then placed under the funnel, the filter pierced with a platinum wire, and the precipitate rinsed with 2½ per cent. ammonia solution into the basin, washing the filter copiously. The precipitate is now dissolved by stirring, the liquid poured into a beaker, which is rinsed with 2½ per cent. ammonia, and as much more of the latter is added as will make up the volume to about 100 c.c.; about 15 c.c. of chloride of magnesium mixture is then dropped in, stirring meanwhile, and after allowing it to remain covered up for two hours, it is treated as in *aa*.

cc. Second modification by P. WAGNER;† this is based upon the fact (ascertained by GILBERT‡ and by E. RICHTERS §), that in the presence of 15 per cent. of nitrate of ammonia about half the usual quantity of molybdenum solution is sufficient to precipitate the whole of the phosphoric acid.

To 25 or 50 c.c. of the phosphate solution contained in a beaker, and in which there is perhaps 0·1 to 0·2 gram of phosphoric acid, sufficient concentrated nitrate of ammonia solution,‖ and also of 5·5 to 6·1 per cent. molybdic acid solution (p. 541 note *) is added so that the total bulk of liquid contains 15 per cent. of nitrate of ammonia and at least 50 c.c. of molybdic acid solution to every 0·1 gram of phosphoric acid. The contents of the beaker are heated to 80° or 90° in a water-bath, put aside for about an hour, filtered, and the precipitate washed with a dilute, acidified solution of nitrate of ammonia.* The precipitate is then dissolved as in *bb*, by 2½ per cent. ammonia, and more of the latter is added so that the volume of the liquid is about 75 c.c.; 10 c.c. of chloride of magnesium mixture is dropped in for each 1·0 gram of phosphoric acid, stirring meanwhile, and the mixture subsequently treated as in *bb*.

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* Zeitschr. f. anal. Chem. 19, 444.

† *Ibid.* 21, 289.

‡ Correspondenzblatt d. Vereins analytischer Chem. 1 Nov. 1878.

§ Dingler's polyt. Journ. 199, 183; Zeitschr. f. anal. Chem. 10, 469.

‖ 750 grams of nitrate of ammonia dissolved in water to make 1 litre.

β. C. Glaser's *Method.*

§ 310.

Of this process, described by C. Glaser,† the author has no personal experience, but as according to the information supplied by Glaser it has constantly proved correct, an account of the process is introduced here. It rests on the fact that phosphoric acid in presence of lime salts, &c., is completely and at once precipitated by magnesia mixture if citrate of ammonia is present, provided there is sufficient sulphuric acid to convert all the lime salts into sulphate and no more citrate of ammonia than is requisite to keep the lime salts dissolved in an alkaline solution. The method is carried out in the following way:

Ammonia is added to the acid solution containing phosphate of lime until a turbidity is produced, and then, preferably by a dropping tube or small pipette, carefully, so much of a 50 per cent. citrate of ammonia solution as is necessary to clear the liquid again. If the reaction is now alkaline, the solution is ready for precipitation. If still acid or neutral, either ammonia or citric acid is added until the point is reached, that is until on adding the last drop of citric acid, the perfectly clear liquid is still decidedly alkaline. This point is reached after a little practice, with 3 or at most 4 c.c. of citric acid solution. To the cooled liquid, the necessary quantity of magnesia mixture ‡ is now added drop by drop, with constant stirring, and then ammonia in large excess. After 6 to 8, or better still 12 hours, the precipitate is collected, washed with 4 per cent. ammonia, dissolved on the filter with dilute (about 15 per cent.) sulphuric acid, and the filtrate precipitated by ammonia with the addition of a little magnesia mixture. After settling (which is generally complete in an hour) it is collected, with the aid of the pump, on asbestos contained in a platinum Gooch's crucible, washed with water containing some ammonia, ignited, and weighed as pyrophosphate of magnesia.§

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* 150 grams of nitrate of ammonia and 10 c.c. of nitric acid dissolved in water to make 1 litre.

† Zeitschr. f. anal. Chem. 24, 178.

‡ C. Glaser gives the following directions for preparing the magnesia mixture:—140 grams of sulphate of magnesia, 150 grams of sulphate of ammonia, and 30 grams of chloride of ammonium, are dissolved in 350 c.c. of 16 per cent. ammonia and 1650 c.c. of water and filtered after standing for several days.

§ The three test analyses communicated by Glaser are entirely satisfactory; but in the author's opinion it remains to be ascertained whether in these cases two errors have not counterbalanced one another. According to previous experience, citrate of ammonia may hold a little phosphate of ammonia and magnesia in solution (as is known of tartaric acid, see Vol. I. p. 316, *e*, *a*), whilst on the other side the precipitate may contain an admixture of sulphate of magnesia (see Rose's "Handbuch der analyt. Chem." 6th edition, by Finkener, Vol. II. p. 513).

If it is desired to determine volumetrically (by the uranium method) the phosphoric acid in any of the phosphates mentioned in I., more particularly in the case of those poor in ferric oxide, dissolution is effected as in § 308, but hydrochloric acid may be used instead of nitric acid for this purpose. The free acid is then removed as far as possible by evaporation, finally neutralising with potassa or soda, and the solution is treated as in § 313, ββ.

Should the amount of phosphoric acid soluble in citrate of ammonia have to be determined in one of the phosphates given in I., it is treated as in § 315, and the amount left in the insoluble residue is then ascertained. By deducting this from the total phosphoric acid, the proportion soluble in citrate of ammonia is obtained.

II. MANURES CONTAINING PHOSPHORIC ACID IN THE FORM OF COMPOUNDS SOLUBLE IN WATER.

§ 311.

Under this heading are comprised *superphosphates*, the products obtained on treating the phosphates mentioned in I. with sulphuric acid.

These contain in the first place, besides large quantities of sulphate of lime and smaller quantities of unattacked basic phosphate of lime, large proportions of acid phosphate of lime, and under some circumstances free phosphoric acid also; the phosphoric acid in the last two forms is soluble in water, that in the first being insoluble. The superphosphates are, however, not stable substances, for, when kept, the acid phosphate of lime, $CaO,2HO,PO_5$, or the phosphoric acid, $3HO,PO_5$, reacts with the basic phosphate, $3CaO,PO_5$, producing neutral phosphate of lime, $2CaO,HO,PO_5$. As this is insoluble in water, the portion of the phosphate soluble in water diminishes whilst the insoluble portion increases. This change is called "*retrogression* of the superphosphate." Whilst this happens in superphosphates prepared by the action of sulphuric acid on nearly pure basic phosphate of lime, it occurs to a much greater extent in those prepared from crude phosphate rich in ferric oxide or silicate of alumina, especially when these also contain fluoride of calcium, as the latter gives rise to hydrofluoric acid when acted on by sulphuric acid and this decomposes the admixed silicates. The retrogression is then due not only to the reactions already mentioned but also to the formation of insoluble phosphates of iron and alumina.

Phosphoric acid has a different agricultural value according to the state in which it exists—whether soluble in water, "retrograde," or in the unattacked (already insoluble) condition—and in a complete analysis of superphosphate, the phosphoric acid in each of these forms must be separately determined. As however such analyses take up much time and labour, attempts have been made to estimate the agricultural value of superphosphate in a simpler manner. To these attempts are due the terms "soluble phosphoric acid" and "phosphoric acid soluble in citrate." In the following paragraphs all these methods of estimation will be considered, commencing, however, with the determination of moisture.

1. Determination of Moisture.

This is effected as in I., 1 (this vol. p. 539), and as a rule at 100°. As however the sulphate of lime present in large quantity only yields up the whole of its water very slowly at 100°, a constant weight is only obtained after heating for a considerable time.

2. Estimation of the Phosphoric Acid.

a. In the three conditions in which it may occur in Superphosphate.

a. Estimation of the Phosphoric Acid soluble in Water.

§ 312.

aa. Preparation of the Solution.

aa. By washing on a filter.* The superphosphate is triturated with a little water in such a manner that the lumps are completely broken up whilst the coarse, hard pieces are not ground to fine powder; it is then rinsed on to a filter and washed with cold water, until the washings are no longer acid, best by exhaustion with a water pump. If the first filtrate becomes turbid on mixing with the washings, the turbidity is removed by adding a little nitric acid, and the whole is then made up to a known volume and mixed. With finely divided, homogeneous superphosphates, 250 c.c. of solution is prepared from 5 grams of substance, or with less uniform samples 500 or 1000 c.c. from 10 or 20 grams.

ββ. By treatment with water. Although the process described under *aa* is indicated as giving the most accurate results,† yet it is not in use in the German agricultural experimental stations, as it takes up more time. These institutions have rather agreed on the following:‡

20 grams of the superphosphate is mixed with water in a mortar, lightly broken down with a pestle without being finely ground, and rinsed into a litre flask; when this operation is finished, the flask is at once filled up to the mark, left to digest for two hours § at the temperature of the room, with frequent shaking, and filtered through a dry filter. The volume of the undissolved residue is not taken into consideration in the subsequent calculation.

bb. Determining the Content of the Solution.

§ 313.

aa. Gravimetric method. A measured quantity of the solution prepared according to § 312 *aa* or *ββ* is used, containing 0·1 to 0·2 gram of phosphoric acid, determining the latter as in § 309.

ββ. Volumetric Uranium method.‖ As, for precipitating one and the same amount of phosphoric acid, different quantities of uranium solution are required according as the solution contains a salt of lime or not, and ammonia salts are present or not, it must be considered as essential that the phosphoric acid solution by which the uranium solution is standardised, must have as nearly as possible the same composition as the one which is being tested. Upon this basis is founded the following method agreed on by the German Agricultural Experimental Stations, which, however, is only trustworthy for superphosphates containing less than 1 per cent. of phosphoric acid in combination with ferric oxide, or alumina.* In the case of superphosphates not containing appreciably more than 20 per cent. of phosphoric acid soluble in water, 50 c.c. of an acidified solution of acetate of ammonia† is added to 200 c.c. of the solution prepared as in § 312. ββ. As soon as the white precipitate of ferric phosphate and phosphate of alumina thus produced has subsided, it is collected on a dry filter, and the precipitate washed three times with hot water after removing the filtrate, ignited and weighed, one half of the weight being calculated as phosphoric acid in combination with ferric oxide and alumina. With superphosphates which contain appreciably more than 20 per cent. of phosphoric acid soluble in water, only 100 c.c. of the solution is taken, adding 100 c.c. of water and 50 c.c. of the acidified solution of acetate of ammonia.

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* See Zeitschr. f. anal. Chem. 7, 304, and 12, 276.

† Zeitschr. f. anal. Chem. 12, 275.

‡ *Ibid.* 21, 288.

§ With many superphosphates, the duration of digestion exerts a not unimportant effect on the result, the prescribed time, therefore, must not be arbitrarily altered; compare ABESSER, JANI, and MÄRCKER, *ibid.* 12, 275.

‖ As the uranium method already described in Vol. I. p. 312, has meanwhile undergone important improvements (see especially ABESSER, JANI and MÄRCKER, Zeitschr. f. anal. Chem. 12, 254), somewhat must here be added to what was said in that place.

The uranium solution employed is one of nitrate of uranium,‡ the titration being effected by using 50 c.c. of the solution filtered off (but not diluted with washings) from the precipitate of phosphates of iron and alumina, and consisting of 40 c.c. of the original solution with 10 c.c. of acetate of ammonia solution (see Vol. I. p. 313). After brisk boiling over a naked flame, or heating it on a boiling water-bath, the end reaction is ascertained by adding finely powdered ferrocyanide of potassium, or a freshly prepared solution of it, to the solution on a white porcelain slab. To prevent a separation of phosphate of lime from the solution, it is advisable to add the approximately necessary quantity of uranium solution in the cold and heat afterwards. The effective value of the uranium solution is ascertained by means of a solution of superphosphate containing about 16 per cent. of phosphoric acid and free from iron, or by a solution of approximately equal content of phosphoric acid prepared by treating pure basic phosphate of lime with a corresponding quantity of sulphuric acid. In titrating the uranium solution, the same proportion must be maintained between the phosphoric acid solution and that of the acetate of ammonia, as in the analysis of the superphosphate. The content of phosphoric acid in the titrating solution is determined by the molybdenum method.

§ 314.

γγ. *Acidimetric method.* The acidimetric methods of superphosphate analysis are founded upon the determination of its acidity by a titrated alkaline liquid. Although the aqueous solution of superphosphate generally contains only acid phosphate of lime along with sulphate of lime, it must be remembered that free phosphoric acid, and, in badly prepared articles, free sulphuric acid, may also be present. As in such cases, the direct titration with caustic soda will not yield accurate results, the acidimetric method for determining the value of superphosphate must be founded upon another basis. The method first proposed, that of A. Mollenda,* is based upon the precipitation of lime from the solution by means of oxalate of soda or oxalate of ammonia, at the boiling temperature, and titration of the solution, now containing only acid alkali phosphate, by normal, or better, N/2, caustic soda, using phenolphthalein as indicator. The end reaction (violet coloration) appears as soon as the acid alkali phosphate (mono-sodium phosphate for example) is changed into the so called neutral salt (di-sodium phosphate). 1 equiv. of soda corresponds with 1 of phosphoric acid. If the superphosphate solution contains free acid, lime water or carbonate of soda is added until a slight turbidity, persistent when stirred, is produced, the free phosphoric acid being thereby converted into acid phosphate of lime, whilst free sulphuric acid becomes neutral sulphate. It is now precipitated with the alkali oxalate, and the process carried out as prescribed. It is better to ascertain the necessary amount of lime water or carbonate of soda by a separate experiment, and on the result of this to add to the solution to be titrated only so much of the neutralising agent that it will remain just clear. It is unnecessary to filter off the oxalate of lime. The liquid to which excess of oxalate of ammonia has been added may be titrated directly with a N/2 caustic soda after adding phenolphthalein or phenacetolin. The test analyses given by Mollenda are satisfactory. See also R. T. Thomson.†

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* Zeitschr. f. anal. Chem. 21, 288.

† 100 grams of pure acetate of ammonia and 100 c.c. of acetic acid of sp. gr. 1·039 to 1·040 (*Acetum concentratum*) are dissolved in water, and made up to 1 litre.

‡ 100 grams of nitrate of uranium dissolved in 2820 c.c. of water is mixed with 10 grams of acetate of ammonia to neutralise the small amount of free nitric acid generally present. 1 c.c. of the solution corresponds with 0·005 gram of phosphoric acid.

A. Emmerling's ‡ method, which has not only been thoroughly worked out, but is also adapted for superphosphates containing iron, is founded upon two experimentally established facts, namely—

1. That the phosphoric acid in a solution of superphosphate to which an excess of chloride of calcium has been added is almost entirely thrown down by caustic soda, but only quite completely if the mixture of superphosphate solution and chloride of calcium is allowed to run into the caustic soda, as in that case the liquid is alkaline during the precipitation. If phenolphthalein has been added to the solution, the end reaction appears when 2 equiv. of NaO have been used for 1 of phosphoric acid.

2. The second fact is, that on adding caustic soda to a solution of free phosphoric acid mixed with methyl-orange, the colour changes from violet-red to yellow or orange yellow when all the phosphoric acid is converted into acid phosphate of soda (monosodium phosphate).

For carrying out the method, the following are required:

1. A solution of caustic soda 1 c.c. of which corresponds with 0·005 gram (about) of phosphoric acid (PO_5), calculated on the relation $2(NaO,HO) : PO_5$. In standardising this by means of a N/5 or N/10 hydrochloric acid, the same quantity of phenolphthalein (2 c.c.) should be employed as is used in effecting the phosphoric acid titration.

2. A chloride of calcium solution prepared by dissolving 200 grams of pure dry chloride of calcium in 1 litre of water; the alkaline reaction of the solution must be most carefully neutralised. The amount of normal hydrochloric acid required to neutralise 100 c.c. is ascertained

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* Zeitschr. f. anal. Chem. 22, 155.

† *Ibid.* 24, 232.

‡ Landwirthschaftl. Versuchsstat 1886, p. 429.

by titration, and the remaining 900 c.c. are then correspondingly neutralised.

3. A solution of 1 gram of phenolphthalein in 100 grams of spirit of wine.

4. A solution of methyl-orange prepared by adding small quantities of methyl-orange to water until the solution is a deep orange yellow, and then filtering.

The analysis itself is carried out in the following manner:

200 c.c. of the superphosphate solution prepared in the usual way (§ 312), mixed with 50 c.c. of the chloride of calcium solution, is allowed to run out of a burette into a measured quantity of the caustic soda (diluted with a little water and to which 2 c.c. of phenolphthalein has been added), until the red colour completely disappears. For superphosphates of high percentage, 20 c.c. of the caustic soda is measured out; for those of 10 to 15 per cent., 10 c.c. is taken; and for poorer superphosphates, 5 c.c. The addition of the mixed superphosphates and chloride of calcium solution is carried on rapidly until the colour begins to be weak, but towards the end drop by drop only. The end reaction is attained when every trace of red colour has vanished, and a whitish, yellowish, or faintly brownish, coloration appears. In stirring the liquid while the solution is being dropped in, the formation of froth must be avoided, as this renders it difficult to observe the change of colour. The experiment must be repeated. In this way, the amount of soda required to neutralise any sulphuric acid present, or for converting free phosphoric acid into acid phosphate of soda, is found.

The same number of c.c. of the superphosphate and chloride of calcium mixture, as were required for the last test, or the mean of the two tests, is now measured out, diluted with a little water, 4 to 6 drops of the methyl-orange solution is added, that is an amount sufficient to impart a decided but not too deep violet-red coloration, produced by the free acid present, and the caustic soda is added from a burette until every trace of reddish tinge has completely disappeared and the liquid assumes a yellow or orange colour. This test must also be repeated.

By deducting from the soda solution used in the titration with phenolphthalein, the amount required in the methyl-orange test, we obtain the number of c.c. of the soda solution needed to precipitate the phosphoric acid as basic phosphate of lime (tricalcium phosphate); then, by multiplying this difference by the quantity of phosphoric acid corresponding with 1 c.c., the amount of phosphoric acid in the number of c.c. of superphosphate and chloride of calcium mixture used is found, and from this the amount in the superphosphate solution, taking the proportion as 250 : 200.

The numerous test analyses of **Emmerling** are—also with superphosphates containing iron—satisfactory, the differences compared with the uranium method not exceeding ± 0·3 per cent. The results come out too high rather than too low, about 0·16 per cent. according to **Emmerling**.

β. *Estimation of the "retrograde" and of the unattacked Phosphoric Acid.**

§ 315.

The "retrograde" phosphoric acid may be determined both directly and indirectly. Both methods are based on this, that the phosphoric acid compounds formed by "retrogression" are soluble in a solution of neutral citrate of ammonia, whilst the unattacked phosphates, particularly those of mineral origin, are practically insoluble therein. The direct method is inconvenient, and consequently reference is merely made to the treatise mentioned in the note. The indirect process which will be described here is much more convenient, and by its means the amount of the unattacked phosphoric acid is ascertained at the same time.

Two portions of superphosphate of 2 grams each are weighed out and dissolved in the manner described under "Washing on the Filter" (§ 312). In the residue from the one (*a*), the total amount of the unattacked and retrograde phosphoric acid is determined by dissolving as in § 308 and estimating the phosphoric acid according to § 309. The filter containing the second residue (*b*) is spread on a glass plate, 100 c.c. of a solution of neutral citrate of ammonia, sp. gr. 1·09, is placed in a small wash-bottle, and the contents of the filter are rinsed completely into a small mortar provided with a lip. It is then allowed to settle, the turbid liquid poured into a flask, and the residue in the mortar is ground to a very fine paste and placed in the flask along with the remainder of the citrate of ammonia solution. The mixture, after being left in the flask for half an hour at 30° to 40°, shaking frequently, is filtered, and the contents of the filter are washed twice or thrice with a mixture of equal parts of water and the above-mentioned citrate of ammonia solution, afterwards with water alone. The residue is then dissolved as in § 308, and the "*unattacked phosphoric acid*" in the solution is estimated as in § 309. By deducting the amount thus obtained from the total phosphoric acid found in the residue *a*, the quantity of "*retrograde*" phosphoric acid is ascertained.

b. Shortened Methods for estimating the values of Superphosphate.

a. Estimation of "soluble" Phosphoric Acid.

§ 316.

The term "soluble phosphoric acid" employed in denoting the value of superphosphate (which must not be confounded with the term "phosphoric acid soluble in water," nor with the expression "phosphoric acid soluble in citrate, or assimilable phosphoric acid," to be referred to hereafter in b. β.) was introduced by P. **Wagner**, as also the method of estimating "soluble phosphoric acid." Both definition and process have been adopted by the Agricultural Experimental Stations of Bonn, Darmstadt, Speyer, and Wiesbaden, and the manure manufactories under their control, to assist in the proper valuation of the retrograde phosphoric acid on the one hand, and the phosphoric acid present in precipitated phosphates on the other.* The basis of the method is the fact established by P. **Wagner**, from minute examination of manures, that 100 parts of phosphoric acid in retrograde or precipitated phosphates have an average agricultural value equivalent to 70 parts of phosphoric acid soluble in water, together with his assumption that, by the analytical methods to be described, the sum of the phosphoric acid soluble in water and that of the equivalent portions of precipitated or retrograde phosphoric acid, is extracted and estimated.

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* See **Fresenius**, **Neubauer** and **Luck**, "Zeitschr. f. anal. Chem." 10, 156.

The method of estimating the "soluble phosphoric acid" is as follows: 5 grams of superphosphate ground down fine with dilute citrate solution † is rinsed into a half-litre flask. The mixture is filled up to the mark with dilute citrate solution, left for about 18 hours at the temperature of the room with frequent shaking, and filtered. 50 c.c. of the filtrate is mixed with as much 5·5 to 6·1 per cent. molybdenum solution (this vol. p. 541, note*) that not less than 1 c.c. of the latter is present for each 0·001 gram of phosphoric acid, and to this mixture concentrated nitrate of ammonia solution (this vol. p. 542, note ||) is added in quantity sufficient to make one-fourth of the total volume of the mixture. After being heated for about 20 minutes on the water-bath and then cooled, it is filtered, the precipitate washed with dilute nitrate of ammonia solution (this vol. p. 543, note*), and rinsed back into the beaker with 2½ per cent. ammonia through the pierced filter. The filter is well washed with the same liquid, and into the cold ammoniacal solution, 20 c.c. of chloride of magnesium solution (this vol. p. 541, note §) *is dropped* with constant stirring. After about an hour, the precipitate is collected, washed with 2 per cent. ammonia, dried, and ignited, finally before the blow-pipe.

β. *Estimation of the Phosphoric Acid soluble in Citrate.*

§ 317.

Whilst the recent examinations of manures by P. **Wagner** have shown that 100 parts of the phosphoric acid in precipitated or retrograde phosphate, and also that soluble in citrate of ammonia, are equivalent to 70 parts of phosphoric acid soluble in water, earlier investigations on manures by **Petermann** and other Belgian and French agricultural chemists, led to the conclusion that phosphoric acid soluble in water is of equal value with that soluble in citrate of ammonia.‡ On this basis is founded the following method given by **Petermann** § for estimating the value of superphosphate, which is practised in Belgium and France especially, the object being to bring simultaneously into solution, by the aid of citrate of ammonia, both the phosphoric acid soluble in water and the retrograde phosphoric acid, whence the abbreviated description "phosphoric acid soluble in citrate," to which also the name "assimilable phosphoric acid" is occasionally given.

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* Zeitschr. f. anal. Chem. 25, 272.

† 150 grams of citric acid is dissolved in water in a litre flask and neutralised by ammonia; to the neutralised solution 10 grams of nitric acid is added, the flask filled up to the mark, and the whole mixed. Of this *concentrated* (and permanent) solution, 1 vol. is mixed with 4 vols. of water to produce the *dilute* (and less permanent) solution.

‡ See hereon **Grandeau**, "Handb. f. agriculturchem. Analysen," p. 71; **Brunner**, "Zeitschr. f. anal. Chem." 19, 141.

§ Landwirthsch. Versuchsstat. 24, 327; Zeitschr. f. anal. Chem. 19, 142.

The citrate of ammonia solution employed is one of 1·09 sp. gr., to which has been added 50 c.c. of ammonia per litre. 100 c.c. of this is placed in a small wash-bottle, 2 grams of the superphosphate [*] is rinsed into a porcelain mortar by means of this solution, triturated, rinsed with the remainder of the citrate of ammonia solution into a half-litre flask, and digested for an hour at 35° to 38°, shaking frequently. When cold, it is filled up to the mark with water, shaken, filtered through a dry, double filter (the filtrate is often turbid at first, but afterwards comes through clear), and 100 c.c. of the clear filtrate is precipitated with 60 c.c. of chloride of magnesium mixture (this vol. p. 541, note §), stirring continuously. After 15 hours, it is filtered, and the phosphate of ammonia and magnesia washed with 2·5 per cent. ammonia, ignited, and weighed. According to PETERMANN, the method does not yield absolutely accurate results, but differences of 0·2 to 0·4 per cent. As compared with the difference-method described in § 315, BRUNNER [†] obtained sufficiently concordant results in parallel analyses.

Appreciably differing from these critical remarks was the conclusion arrived at by the meeting of agricultural chemists at Halle, in December 1881, which was to the effect that the methods proposed and employed for estimating phosphoric acid "soluble in citrate," did not even approximately effect their object. Should however this method of estimation be adopted, it was agreed to digest 5 grams of unwashed superphosphate with 100 c.c. of PETERMANN's citrate solution in a 250 c.c. flask for an hour at 40°, fill up to the mark, filter and determine the phosphoric acid in an aliquot portion of the filtrate. In communicating the result, the insufficiency of the method should however be pointed out; [‡] see also Vol. I. p. 316, e *a*.

c. Estimation of the total Phosphoric Acid in Superphosphates.

§ 318.

5, 10 or 20 grams of the superphosphate, according to the degree of homogeneity, is dissolved by warming with nitric acid, treating any difficultly soluble residue with hydrochloric acid, and adding chlorate of potassa for the decomposition of any organic matter present; the whole is made up to 250, 500, or 1000 c.c. according to the quantity taken, mixed, filtered through a dry filter, and the phosphoric acid determined in a quantity of the solution containing from 0·1 to 0·2 gram of phosphoric acid, as in § 309. When hydrochloric acid or chlorate of potassa is used, the portion of the filtrate removed by pipetting must be repeatedly evaporated almost to dryness with nitric acid, the residue treated with nitric acid and water, and the solution filtered.

D. Analysis of Manures whose value is wholly or almost entirely due to their content of Potassium.

§ 319.

To this class belong, chloride of potassium and the sulphate of potassa prepared on a large scale from the waste salt of the Stassfurth and other rocksalt beds, which come to the market in a more or less pure state; the impure salt obtained from the mother liquors, that is, the "crude sulphate of potassa," containing very variable amounts of sulphate of potassa and chloride of potassium, and also the minerals from which the above-named salts or double salts of potassa are made. Such minerals are carnallite, $KCl,2MgCl + 12HO$, containing in a crude state about 16 per cent. of chloride of potassium, besides about 20–25 per cent. of chloride of sodium, 15 to 20 per cent. of kieserite and 2 to 4 per cent. of chloride of magnesium, tachydrite, &c.; further, kainite $KCl,2(MgO,SO_3) + 6HO$, which, as crude kainite, only contains 12 to 13 per cent. of potassa, or reckoned as sulphate, 22 to 24 per cent. of the latter, together with 11 to 12 per cent. of sulphate of magnesia, 12 to 15 per cent. of chloride of magnesium, 37 to 42 per cent. of chloride of sodium, about 2 per cent. of sulphate of lime, 1 to 2 per cent. of insoluble residue, and 5 to 8 per cent. of water. In addition, the preparations poor in chlorine, produced by calcining crude kainite, should be mentioned; these come into the market as "prepared kainite," "crude sulphate of potassa and magnesia," or "sulphate of potassa and magnesia manures," and finally the "pure, crystallised sulphate of potassa and magnesia," containing 38 to 40 per cent. of sulphate of potassa, obtained from kainite by treatment with water.

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[*] In employing the method for precipitated phosphate or mixed manures PETERMANN uses, in the former case, 1 gram, and in the latter 5 grams.

[†] Zeitschr. f. anal. Chem. 19, 143.

[‡] *Ibid.* 21, 291.

As the analysis of potassium salts has already been thoroughly treated of in § 225 (this vol. p. 218), both with reference to a simple estimation of potassa and to complete analysis, this should be referred to.

It is advisable to take so much of the aqueous solution of the salt to be tested as will produce about 0·8 to 1·2 gram of platinochloride of potassium; on multiplying the weight of the latter dried at 130° by 0·3056, the chloride of potassium is obtained. This figure corresponds, according to WATTS'* calculation, with BERZELIUS' equivalent of platinum. If the weight of the double salt dried at 130° is multiplied by 0·30697, the figure given by SEUBERT'S † equivalent, the result will be rather too high, or if 0·3051, the number derived from ANDREWS' ‡ equivalent for platinum be taken, the result will be somewhat too low for chloride of potassium, as shown by the author's investigations.§

E. Analysis of Manures, the value of which depends solely or almost entirely on the Nitrogen they contain.

In this category, rank salts of nitric acid, and before all others Chili saltpetre, ammonia salts, and such nitrogenous manures of organic origin as contain so little of other manurial substances (potassa and phosphoric acid) that the value of the latter is barely, if at all, taken into account; such, for example, as dried blood, hornmeal, &c. As the methods of estimating nitrogen vary with the state of combination in which it occurs, they must be described separately.

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* Zeitschr. f. anal. Chem. 9, 156.

† Annal. d. Chem. 207, 31.

‡ Annal. d. Chem. u. Pharm. 85, 255.

§ Zeitschr. f. anal. Chem. 21, 234.

I. Chili Saltpetre.*

§ 320.

Although pure nitrate of soda contains 63·52 per cent. of nitric acid, or 16·502 of nitrogen, Chili saltpetre—containing as it does a little chloride of sodium, sulphate of soda, insoluble residue, water, &c.—is only guaranteed by the manure merchant to contain 15 to 15·5 per cent. of nitrogen.

Of the methods for estimating the nitric acid in Chili saltpetre, given in § 149 (Vol. I. p. 390), the most suitable of all is Reich's (described in Vol. I. p. 391), that is, heating to redness with quartzose sand, as being quick, simple, and yielding very good results. This can also be carried out in the manner described by Märcker and Abesser,† a modification of Reich's original plan mentioned above. A weighed quantity of powdered Chili saltpetre (about 1 to 1·5 gram) is carefully mixed with about a sevenfold amount of quartz sand, which has been previously extracted with hydrochloric acid and washed and ignited; it is then heated for 4 hours in a crucible, which has been weighed with its contents, in such a manner that only about one-third of the crucible is heated to redness. After weighing, it is heated for half-an-hour longer to see that there is not any further loss of weight. From the total loss (nitric acid + water) observed, the water in the Chili saltpetre must be deducted in order to find the amount of nitric acid. This, as a rule, can be ascertained by drying quickly at about 130°, but under certain circumstances, for instance if it is adulterated with kainite, it must be heated to redness.

Of course other methods may be employed for determining the nitric acid in Chili saltpetre. Many of these have already been described in § 149‡ (Vol. I. p. 390), others are of more recent date. Although Reich's method, already mentioned, is, in respect of its simplicity and accuracy, sufficient for determining the value of Chili saltpetre, still other processes which are largely used for the same purpose must also be mentioned, as well as a few new ones which are useful in the analysis of mixed manures.

Persoz's method (Vol. I. p. 391) is frequently employed in place of Reich's for determining the value of Chili saltpetre. It consists in heating the anhydrous nitrate with anhydrous dichromate of potassa, and estimating the nitric acid from the loss in weight. E. Pfeiffer § recommends the use of 3 to 4 parts of dichromate of potassa for each part of nitrate, as the evolution of the nitric acid is thereby facilitated, and advises the placing of a triangle of thin platinum wire between the platinum crucible and the lid in order to allow space for the vapours to escape. The temperature should only be raised to an incipient, dull, red heat, and the operation is ended when the mass is in a state of quiet fusion. If green particles of chromic oxide are observed on the surface of the fused mass after cooling, or on the lid from spurtings, the experiment must be rejected. Instead of dichromate of potassa, many recommend the use of equal parts of chromate and dichromate of potassa.*

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* In this Appendix, those newer methods of nitric acid estimation will also be described, which, if not exactly necessary for determining the value of Chili saltpetre, are to be kept in mind in the case of mixed manures.

† Zeitschr. f. anal. Chem. 12, 281.

‡ J. M. Eder (Zeitschr. f. anal. Chem. 16, 267) has made a valuable critical examination of most of the methods therein mentioned.

§ Arch. Pharm. (3), 13, 539; Zeitschr. f. anal. Chem. 18, 597.

A method based upon a new principle is recommended by A. WAGNER;† it consists in fusing the nitrate with carbonate of soda and chromic oxide in a glass tube filled with carbonic acid, lixiviating the fused mass, and determinating in the filtrate the chromic acid formed, the nitric acid being calculated from this. This process gives good results,‡ but is much more complicated than the system of REICH or PERSOZ. The nitric oxide evolved can be collected and measured, as a means of controlling the operation, or—as in SCHLÖSING'S method (Vol. I. p. 395)—converted into nitric acid.

All the methods more recently recommended for the estimation of nitric acid are only modifications of those given in § 149, or of the process originated by WALTER CRUM, described in this vol. p. 446. They are for the most part founded upon the conversion of nitric acid into nitric oxide, that is upon the principle detailed in Vol. I. p. 392, under *d*; and many are merely modifications of SCHLÖSING'S method (Vol. I. p. 395), which had also previously been modified in various ways (Vol. I. p. 396, and Vol. II. p. 42).

Above all, SCHLÖSING § has himself made important alterations in his process, and imparted to it a high degree of simplicity both in working it and in the calculation, by collecting over water and measuring the nitric oxide gas resulting, on the one hand, from the action of a known quantity of nitric acid on ferrous chloride, and on the other hand from the unknown amount of nitric acid in the substance examined under identical circumstances. As the first experiment gives the amount of nitric acid (or the nitrogen contained therein) corresponding with 1 c.c. of nitric oxide gas under the existing conditions, so in the second experiment the amount of unknown nitric acid or nitrogen can be deduced directly from the volume of nitric oxide gas produced, the pressure, degree of moisture, and temperature of both volumes of gas being the same. The other sources of error, inherent in the measurement of nitric oxide over water (the slight solubility of nitric oxide in water, influence of the oxygen in the air dissolved in the water), are thereby excluded, and this the more completely, the greater the care taken that the volumes of nitric oxide produced from the known and the unknown quantities of nitric acid shall be approximately equal or not differ to any great extent.

SCHLÖSING advised the use of a special apparatus for his modified method, especially a pneumatic trough fitted in a special manner, which fulfils all requirements; this is depicted in GRANDEAU'S "Handbuch," p. 34. The author however considers it more to the purpose to describe here (see Fig. 129) P. WAGNER'S ‖ slightly modified form of that apparatus, as it can be built up out of vessels ordinarily in use in the laboratory.

The process to be followed in estimating Chili saltpetre is as under: 40 c.c. of a solution of ferrous chloride, containing about 200 grams of iron per litre, is introduced into a 250–300 c.c. flask *a*, along with 40 c.c. of hydrochloric acid of sp. gr. 1·1. A few c.c. of the same acid is then poured into a tap-funnel *b*, the tube of which, drawn out to a fine point, reaches into the bulb of the flask but does not dip into the liquid. The glass tap is opened in order to drive out the air from the tube by means of the acid, but closed again before the whole of the acid has run through. The tube *c*, for removing the evolved gas, dips into the water in a glass trough about 24 cm. wide and 20 cm. deep, into which fresh cold water can be passed through the neck *e*, in order to drive out the water, warmed and contaminated by hydrochloric acid during the operation, through the bent glass tube projecting through the opposite neck *f*. In the trough there are four or more glass cylinders, graduated to ½ or 1 c.c. and filled with water, suspended from a wire holder, with rings at the top and clips in the middle. None of these graduated tubes should be placed over the upward inclined end of the gas-tube *c*, at the commencement. The contents of the flask *a* are now heated to boiling and kept boiling until all the air is driven out, which may easily be ascertained by sliding a test tube filled with water over the end of the gas-tube *c*. One of the graduated cylinders is now placed over the gas-tube *c*; 10 c.c. of the normal nitrate solution,

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* P. WAGNER, Chemiker-Zeitung, 1883, p. 1710.

† Dingl. polyt. Journ. 200, 120, and 201, 420; Zeitschr. f. anal. Chem. 11, 91 and 314.

‡ See also EDER (last reference, p. 287).

§ GRANDEAU'S "Handb. d. agriculturchem. Analysen," German edition, p. 31.

‖ Chemiker-Zeitung, 1884, p. 651; Zeitschr. f. anal. Chem. 23, 559.

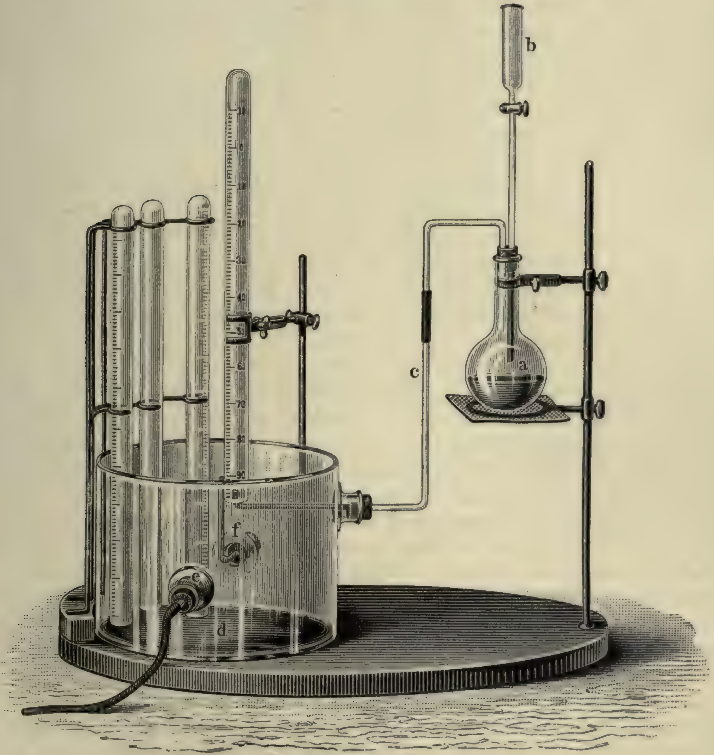

Fig. 129.

containing precisely 33 grams of pure nitrate of soda per litre, is poured into the funnel-tube *b*, and the tap arranged so that the normal solution drops slowly into the iron solution, which is kept constantly boiling. When this is run in, all except a slight residue, the funnel is filled up twice with hydrochloric acid of sp. gr. 1·1; and this is allowed to drop in also until only sufficient remains to fill the tube. When this is accomplished the first operation is complete. Now, keeping the contents of *a* still boiling, the graduated cylinder is moved on one side, another is put in its place, and 10 c.c. of the solution of Chili saltpetre to be tested (which must also contain 33 grams for litre) is put into the funnel *b*, and the process carried out as before, finally washing out the funnel twice with hydrochloric acid. In this way, without exhausting the ferrous chloride solution, six or seven more estimations can be made, followed by a final control estimation with the normal nitrate solution. When this is completed, the glass tap is opened to allow the air to enter *a*, and the lamp is removed.

The graduated cylinder containing the nitric oxide has meanwhile been placed in a glass cylinder about 44 cm. high and 15 cm. wide, in which it is held fast by brass clips fastened to the edge of the glass cylinder; the water displaced by the graduated cylinder in sinking runs off through a side opening. As soon as it is certain that the temperature of all the graduated cylinders and their contents are identical the gas volumes are read off.

By proceeding as above, the percentage of nitrate of soda in Chili saltpetre may be calculated by the following proportion: As the amount of nitric oxide gas evolved from 0·33 gram of pure nitrate of soda is to the nitric oxide gas evolved from 0·33 gram of the Chili saltpetre tested, so is 100 to x. If on the other hand unequal quantities of pure nitrate of soda and the substance to be tested have been taken, the simplest way is to calculate the amount of nitric acid or nitrogen corresponding with 1 c.c. of the nitric oxide obtained from the former, multiplying the value thus found by the number of c.c. of nitric oxide yielded by the unknown quantity of nitric acid. None of the other modifications of SCHLÖSING's original method allow of such rapid working as the one just described. It will suffice therefore to point out the principles upon which they are founded.

C. BÖHMER* advises a gravimetric estimation of the nitric oxide by collecting it in a Liebig's potash bulb, filled with a concentrated solution of chromic acid; E. WILDT and A. SCHIEBE † reconvert the nitric oxide into nitric acid and estimate this by titration, using for that purpose an apparatus which does away with the mercury trough. They consider that their method is preferable to measuring the nitric oxide gas, more particularly in cases where the admixture of other inert gases along with the nitric oxide is to be feared, as in the examination of the sap of plants. WARINGTON ‡ removes the air from the decomposing vessel, as SCHLÖSING had also already proposed, by means of a current of carbonic acid which is passed through a small flask containing a little water and immersed in a bath of chloride of calcium heated at 140°; the nitric oxide is collected over mercury, treated with caustic potash, and finally absorbed by a saturated solution of ferrous chloride. He particularly recommends his method for the accurate estimation of small quantities of nitric acid. WILFARTH[*] converts the nitric oxide into nitric acid by a solution of peroxide of hydrogen in alkali of known strength, in order to estimate the acid by titration.

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* Zeitschr. f. anal. Chem. 22, 20.

† *Ibid.* 23, 151.

‡ *Ibid.* 23, 547.

Various modified methods based upon the principle mentioned in § 149 (Vol. I. p. 397), namely, conversion of the nitric acid into ammonia, have been suggested, and may be briefly referred to in this place. Such are: that proposed by E. PUGH and modified by O. v. DUMREICHER,[†] in which stannous chloride solution is employed, and those of J. WEST-KNIGHT's[‡] and B. KINNEAR,[§] who used zinc and sulphuric acid.

WALTER CRUM's method for the determination of nitric acid, and LUNGE's nitrometer for carrying out the process, have already been thoroughly described in § 271, 2 (this vol. p. 446). According to WARINGTON's investigations,[||] this method is particularly adapted for estimating small quantities of nitric acid, but in presence of large amounts of organic matter it yields results which are too low; this opinion, however, conflicts with LUNGE's experience.[¶] Recently SHEPHERD[**] has recommended the use of the nitrometer for determining nitric acid in manures, and as reference must be made to this paragraph when treating of the examination of mixed manures, the method will be described here in detail. In manures containing about 5 per cent. of nitric acid, only 0·2 gram, and of those with less than 1 per cent. of nitric acid, 2 to 3 grams of substance are taken. The extract, prepared with boiling water, is concentrated to a small bulk and placed in the nitrometer; the removal of the chlorine by sulphate of silver is unnecessary, and the volume of liquid should be so small as not to exceed 5 c.c. including the washings. To the completely cooled liquid in the nitrometer, twice its volume of pure concentrated sulphuric acid is *carefully* added, mixing the acid with the aqueous liquid by gently shaking; if necessary, any carbonic acid which may be evolved is allowed to escape by momentarily opening the glass taps, and the whole is then shaken strongly in order to evolve the nitric oxide. The reaction is complete in a few minutes; the apparatus is then left to cool and read off. By making comparative tests under the same conditions, using nitrate solutions of known strength, the pressure of the air and temperature may also be disregarded, the calculation being made as in SCHLÖSING's new method. The question of the influence exercised by organic substances on the results requires further investigation.

II. SALTS OF AMMONIA.

The estimation of ammonia in ammonia salts is performed as a rule either by distillation with the addition of calcined magnesia, or by separating and measuring the nitrogen in it according to the method which KNOP terms azotimetry.

a. By Distillation.

§ 321.

This method has already been described in § 99, 3. (Vol. I. p. 178), and, with respect to the estimation of ammonia in soils, in § 302, *b*.

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[*] Zeitschr. f. anal. Chem. 23, 587.

[†] *Ibid.* 20, 290.

[‡] *Ibid.* 22, 572.

[§] *Ibid.* 25, 224.

[||] *Ibid.* 19, 85.

[¶] *Ibid.* 19, 208.

[**] *Ibid.* 25, 270.

Here it may be noted, that not only with mixed manures, but also with ammonia salts prepared on the large scale, and often containing thiocyanate of ammonium, the distillation must always be made with calcined magnesia and never with hydrate of potassa or soda, as ammonia is produced * by the action of the alkalies on the nitrogen contained in the thiocyanogen, distillation with magnesia, moreover, yields accurate results in presence of phosphates; † percussive ebullition of the ammoniacal liquid can be avoided by passing steam through the liquid instead of heating directly (**Rüdorff** ‡).

With regard to receivers for the titrated acid, it is of course unnecessary to adhere strictly to the form described in § 99, 3., but care must always be taken that the ammoniacal distillate does not come into contact with cork or caoutchouc, as both of these retain a little of it. **Knublauch** § recommends the apparatus shown in Fig. 130 as highly efficient.

a is the distilling flask of 200 to 250 c.c. capability, furnished with the tube *b* which leads to the absorption apparatus *e*; this is in the form of a flask without a bottom, 4 cm. in diameter below and turned out into a lip at several places on the rim so as to assist in distributing the bubbles of gas evolved. The vessel *e* is suspended in the glass cylinder *c* by a cork slab *d* keyed to its neck, so that *e* is a few mm. above the bottom. In *c*, the measured quantity of titrated acid is placed together with so much water that the vessel *e* dips into it about 1 cm. Finally *c* is placed in an outer glass vessel *g* filled with water for condensing. After distilling down the contents of *a* to $\frac{1}{2}$ or $\frac{1}{3}$, so as to drive off all the ammonia, the stopper is removed from *e*, *c* is taken out of the cooler, and when quite cool the excess of acid is titrated without removing *e*. In examining sulphate of ammonia, 20 grams are dissolved to 500 c.c., and 25 c.c. (equivalent to 1 gram) is employed for the distillation; 10 c.c. of water are requisite for rinsing the sides of the flask *a*. If 20 c.c. of normal sulphuric

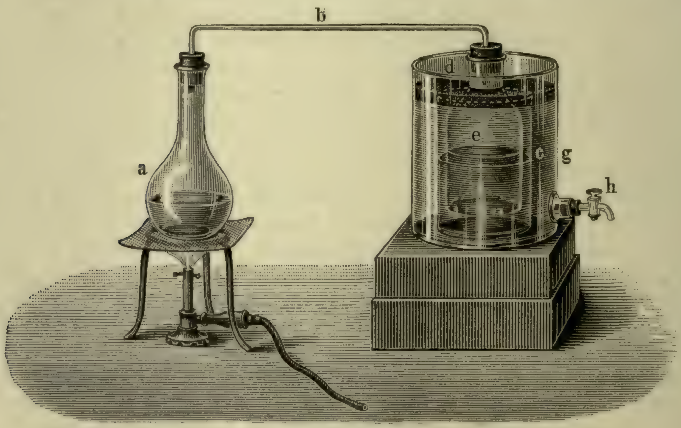

Fig. 130.

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* See **Esilman**, Zeitschr. f. anal. Chem. 14, 94.

† See **Märcker**, *ibid.* 10, 277.

‡ *Ibid.* 12, 440.

§ *Ibid.* 21, 161.

acid is used, then about 6 c.c. of normal soda will be required for the final neutralisation of the excess. KNUBLAUCH, to liberate the ammonia, introduced into the contents of *a* a little solid caustic alkali wrapped in filter paper; the paper swimming on the surface facilitates quiet boiling. From what has been previously said, however, it is evident that caustic alkali can only be employed if thiocyanogen and other nitrogenous organic compounds are absent. According to THOMSON'S* investigations, the best indicators for ammonia titrations are litmus (or the preparation of litmus mentioned in this vol. p. 533, footnote), methyl-orange, or phenacetolin. Rosolic acid is not so good, whilst phenolphthalein is unsuitable.

b. Azotimetric Method.

§ 322.

The azotimetric method to which reference has already been made in this vol. p. 533, is based upon the reaction which takes place when an excess of alkali hypobromite acts on ammonia, as represented by the equation $3(NaO,BrO) + 2NH_3 = 2N + 6HO + 3NaBr$. All the nitrogen of the ammonia is liberated and can be measured. The method is here described in its most complete form as given in one of his latest works† by W. KNOP, who first proposed it. The apparatus employed for the operation is shown in Fig. 131.‡

a. The decomposing vessel in which the solution of hypobromite of soda is allowed to act on the ammonia salt is 10 to 11 cm. high, 5 cm. in diameter, and is closed by a hollow glass stopper continued upwards as a strong glass tube *b*, 8 to 9 cm. long and 2 cm. in diameter, which can be closed above by a glass tap, the latter being connected with a strong tapering glass tube fused on to the upper external part of the tap. The wide tube is packed tightly with coarse glass beads which are prevented from falling into the decomposing vessel by a loose ball of fine platinum wire. The vessel *a* is suspended in the glass cylinder *dd*, 50 c.c. high and 18 c.c. in diameter and containing cold water, by means of a strong metal rod *c*, carrying below a metal plate fixed at right angles for *a* to rest on, and a spring metallic clip higher up. The metal rod can be raised or lowered through a socket, and the whole is fixed in position by a screw clamp. If this is removed, the support for the decomposing vessel still hangs from the metal ring at the top of *dd* on two short, stout steel pins, from which it can easily be removed and as easily replaced.

Attached to the metal ring on *dd* by a screw is also the holder of the U-tube *e*, one of whose limbs is graduated. After removing the screw and taking away the stop-cock *f* and the caoutchouc tube affixed to the ungraduated limb of the U-tube, for the purpose of letting the water out of it, the U-tube itself can be lifted out for cleaning it, or when necessary for renewal of the caoutchouc tubing. The graduated, and the plain, rather longer limb of the U-tube—which should extend a few centimetres above the surface of the water in *dd* so as to be able to fill the tube itself with distilled water—can be joined together below by a caoutchouc tube as shown in the drawing. The U-tube can also be made in one piece, to simplify the repairs of the apparatus which are occasionally necessary. On a short tube projecting from the bottom of the plain limb of the U-tube is fitted a 20 cm. length of caoutchouc tube, the free end of which, when the U-tube is lowered into the vessel *dd*, is drawn by a hook through the tubulure *g* and connected with the glass tube of the tap *f* previously passed through a cork soaked in melted paraffin, the cork being then inserted in the tubulure *g*. The tube *h* connecting the graduated limb of the U-tube with the vessel *a* is of thick, soft caoutchouc with an internal diameter of about the size of a large knitting-needle. It must be long enough to allow of *a* being removed from the water in the vessel and placed on the table beside *dd* without stretching the tube at all. With such a length of tube, no alteration in its volume is to be feared, and the shaking and reversing of *a* can be conveniently effected outside the vessel *dd*.

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* Zeitschr. f. anal. Chem. 24, 225.

† *Ibid.* 25, 301.

‡ For other apparatus which differ more or less from this in construction, see P. WAGNER, Zeitschr. f. anal. Chem. 13, 383, and 15, 250; SOXHLET, *ibid.* 16, 81; GAWALOVSKI, *ibid.* 18, 244, and 24, 61; C. MOHR, *ibid.* 23, 26; MOSSALKI, Bull. Soc. Chim. de Paris, 40, 18.

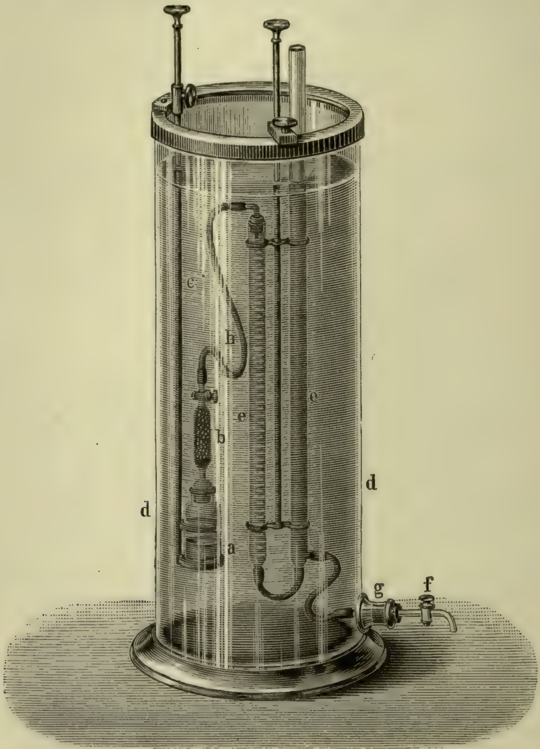

Fig. 131.

The *process* is carried out as follows:

1. 15·2422 grams of pure anhydrous chloride of ammonium is

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* In the figure, the U-tube has been placed on one side to allow the form and arrangement of the vessel *a* to be seen. Actually, when the operator has the U-tube broadside facing him, the glass tap *f* is 90° to the right.

dissolved and made up to 1000 c.c.; 10 c.c. of this solution contain 0·040 gram of nitrogen.

2. 20 grams of the ammonia salt to be tested if sulphate of ammonia, or 16 grams if sal-ammoniac, is dissolved, and made up to 1000 c.c.

3. After loosening the screw on *c*, *a* with its support is taken out of the vessel, *a* is placed on the table near the azotimeter, the stopper taken out, inverted, and through the funnel-shaped opening in the stopper, the tap being open, as much brominated soda solution * is poured from a measured quantity of 50 c.c. as will be sufficient to thoroughly wet the glass beads, the remainder of the 50 c.c. being poured into the vessel *a*, and after the greased stopper has been replaced in *a*, it is left to stand until no more lye drips from the beads; then by means of a pair of forceps a glass tube of suitable size and closed at one end, containing 10 c.c. of the chloride of ammonium solution of known strength, is put in the lye,† the stopper is again inserted, and *a* is connected with the graduated limb of the U-tube by means of the caoutchouc tube, the tap of *b* being left open; *a* and the caoutchouc tube are then immersed in the cold water in *dd* by suspending the support on the two metal studs already mentioned, and left for 20 minutes, taking care that the water is of the same height in both limbs, the height being noted. A small movable plate painted one half white and the other black, serves for the better observation of the level. The temperature of the water in *dd* should not differ appreciably from that of the surrounding air. About 30 c.c. of water is now allowed to run out of *f*, and *a* is taken out of the water and inclined slightly so that a little of the solution of the ammonia salt runs out and the evolution of gas goes on slowly. The small quantity of gaseous ammonia carried off is absorbed and decomposed by the hypobromite adhering to the glass beads. The further admixture of the two liquids is effected in the same way. When the evolution of gas slackens, the tap on *b* is closed and the apparatus shaken, repeatedly inverting *a*. The tap *b* is then opened again and *a*, together with the tubing, is put into the water, moving them up and down to mix the water; it is then fixed at the lowest possible point and left for 20 minutes, when the water is drawn off from *f* until the level of the water in both limbs of the U-tube is the same, and the number of c.c. of nitrogen gas evolved is then read off. This amount—about 32 c.c.—corresponds with 0·040 gram of nitrogen at the barometric pressure, and temperature of the cooling water.

4. The solution No. 2 is then examined in the same manner and the content of nitrogen in the ammonia salt used for this second solution is calculated on the basis of the proportion between volume and weight of nitrogen found in 3. If, in 3, for example, 33 c.c., and in 4. 30 c c. of nitrogen have been obtained, it follows that the weight of nitrogen in 10 c.c. of the No. 2 is

$$33 \text{ c.c.} : 0{\cdot}040 \text{ gram N} = 30 \text{ c.c.} : x, \quad \therefore\ x = 0{\cdot}03636 \text{ gram.}$$

Should the experiment in 4. result in the production of a volume of nitrogen differing considerably from that obtained in 3., the experiment

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* To prepare this, 100 grams of hydrate of soda is dissolved in 1250 c.c. of water strongly cooled, 25 c.c. of bromine is added, and the whole mixed. The liquid must be protected from the action of light.

† P. Wagner recommends fusing the cylinder containing the ammonia salt to the bottom of the decomposing flask (Zeitschr. f. anal. Chem. 15, 250).

I.—*Table of the weight in milligrams under pressures of* 720 *to* 770 *mm. mercury*

	Mм.												
Temperature on the Centigrade Scale.	720	722	724	726	728	730	732	734	736	738	740	742	744
10°	1·13380	1·13699	1·14018	1·14337	1·14656	1·14975	1·15294	1·15613	1·15932	1·16251	1·16570	1·16889	1·17208
11°	1·12881	1·13199	1·13517	1·13835	1·14153	1·14471	1·14789	1·15107	1·15424	1·15742	1·16060	1·16378	1·16696
12°	1·12376	1·12693	1·13010	1·13326	1·13643	1·13960	1·14277	1·14593	1·14910	1·15227	1·15543	1·15860	1·16177
13°	1·11875	1·12191	1·12506	1·12822	1·13138	1·13454	1·13769	1·14085	1·14401	1·14716	1·15032	1·15348	1·15663
14°	1·11369	1·11684	1·11999	1·12313	1·12628	1·12942	1·13257	1·13572	1·13886	1·14201	1·14515	1·14830	1·1514
15°	1·10859	1·11172	1·11486	1·11799	1·12113	1·12426	1·12739	1·13053	1·13366	1·13680	1·13993	1·14306	1·14620
16°	1·10348	1·10658	1·10971	1·11283	1·11596	1·11908	1·12220	1·12533	1·12845	1·13158	1·13470	1·13782	1·14095
17°	1·09828	1·10139	1·10450	1·10761	1·11073	1·11384	1·11695	1·12006	1·12317	1·12629	1·12940	1·13251	1·13562
18°	1·09304	1·09614	1·09924	1·10234	1·10544	1·10854	1·11165	1·11475	1·11785	1·12095	1·12405	1·12715	1·13025
19°	1·08774	1·09083	1·09392	1·09702	1·10011	1·10320	1·10629	1·10938	1·11248	1·11557	1·11866	1·12175	1·12484
20°	1·08246	1·08554	1·08862	1·09170	1·09478	1·09786	1·10094	1·10402	1·10710	1·11018	1·11327	1·11635	1·11943
21°	1·07708	1·08015	1·08322	1·08629	1·08936	1·09243	1·09550	1·09857	1·10165	1·10472	1·10779	1·11086	1·11393
22°	1·07166	1·07472	1·07778	1·08084	1·08390	1·08696	1·09002	1·09308	1·09614	1·09921	1·10227	1·10533	1·10839
23°	1·06616	1·06921	1·07226	1·07531	1·07836	1·08141	1·08446	1·08751	1·09056	1·09361	1·09666	1·09971	1·10276
24°	1·06061	1·06365	1·06669	1·06973	1·07277	1·07581	1·07885	1·08189	1·08493	1·08796	1·09100	1·09404	1·09708
25°	1·05499	1·05801	1·06104	1·06407	1·06710	1·07013	1·07316	1·07619	1·07922	1·08225	1·08528	1·08831	1·09134
	720	722	724	726	728	730	732	734	736	738	740	742	744
	Mм.												

of one cubic centimetre of Nitrogen

and at temperatures between 10° *and* 25°.

Mm.													Temperature on the Centigrade Scale.
746	748	750	752	754	756	758	760	762	764	766	768	770	
1·17527	1·17846	1·18165	1·18484	1·18803	1·19122	1·19441	1·19760	1·20079	1·20398	1·20717	1·21036	1·21355	10°
1·17014	1·17332	1·17650	1·17168	1·18286	1·18603	1·18921	1·19239	1·19557	1·19875	1·20193	1·20511	1·20829	11°
1·16493	1·16810	1·17127	1·17444	1·17760	1·18077	1·18394	1·18710	1·19027	1·19344	1·19660	1·19977	1·20294	12°
1·15979	1·16295	1·16611	1·16926	1·17242	1·17558	1·17873	1·18189	1·18505	1·18820	1·19136	1·19452	1·19768	13°
1·15459	1·15774	1·16088	1·16403	1·16718	1·17032	1·17347	1·17661	1·17976	1·18291	1·18605	1·18920	1·19234	14°
1·14933	1·15247	1·15560	1·15873	1·16187	1·16500	1·16814	1·17127	1·17440	1·17754	1·18067	1·18381	1·18694	15°
1·14407	1·14720	1·15032	1·15344	1·15657	1·15969	1·16282	1·16594	1·16906	1·17219	1·17531	1·17844	1·18156	16°
1·13873	1·14185	1·14496	1·14807	1·15118	1·15429	1·15741	1·16052	1·16363	1·16674	1·16985	1·17297	1·17608	17°
1·13335	1·13645	1·13955	1·14266	1·14576	1·14886	1·15196	1·15506	1·15816	1·16126	1·16436	1·16746	1·17056	18°
1·12794	1·13103	1·13412	1·13721	1·14030	1·14340	1·14649	1·14958	1·15267	1·15576	1·15886	1·16195	1·16504	19°
1·12251	1·12559	1·12867	1·13175	1·13483	1·13791	1·14099	1·14408	1·14716	1·15024	1·15332	1·15640	1·15948	20°
1·11700	1·12007	1·12314	1·12621	1·12928	1·13236	1·13543	1·13850	1·14157	1·14464	1·14771	1·15078	1·15385	21°
1·11145	1·11451	1·11757	1·12063	1·12369	1·12675	1·12982	1·13288	1·13594	1·13900	1·14206	1·14512	1·14818	22°
1·10581	1·10886	1·11191	1·11496	1·11801	1·12106	1·12411	1·12716	1·13021	1·13326	1·13631	1·13936	1·14241	23°
1·10012	1·10316	1·10620	1·10924	1·11228	1·11532	1·11835	1·12139	1·12443	1·12747	1·13051	1·13355	1·13659	24°
1·09437	1·09740	1·10043	1·10346	1·10649	1·10952	1·11255	1·11558	1·11861	1·12164	1·12467	1·12770	1·13073	25°
746	748	750	752	754	756	758	760	762	764	766	768	770	
Mm.													

II.—*Table of Absorption of Nitrogen*

in 60 *c.c. of the decomposing liquid* (50 *c.c. of hypobromite lye and* 10 *c.c. of water*) *the lye being of sp. gr.* 1·1, *and of such a strength that* 50 *c.c. corresponds with* 0·200 *gram of nitrogen, in the evolution of from* 1 *to* 100 *c.c. of gas.*

Evolved .	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Absorbed .	0·06	0·08	0·11	0·13	0·16	0·18	0·21	0·23	0·26	0·28	0·31	0·33	0·36	0·38	0·41	0·43	0·46	0·48	0·51	0·53
Evolved .	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Absorbed .	0·56	0·58	0·61	0·63	0·66	0·68	0·71	0·73	0·76	0·78	0·81	0·83	0·86	0·88	0·91	0·93	0·96	0·98	1·01	1·03
Evolved .	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Absorbed .	1·06	1·08	1·11	1·13	1·16	1·18	1·21	1·23	1·26	1·28	1·31	1·33	1·36	1·38	1·41	1·43	1·46	1·48	1·51	1·53
Evolved .	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80
Absorbed .	1·56	1·58	1·61	1·63	1·66	1·68	1·71	1·73	1·76	1·78	1·81	1·83	1·86	1·88	1·91	1·93	1·96	1·98	2·01	2·03
Evolved .	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
Absorbed .	2·06	2·08	2·11	2·13	2·16	2·18	2·21	2·23	2·26	2·28	2·31	2·33	2·36	2·38	2·41	2·43	2·46	2·48	2·51	2·53

must be repeated, using a correspondingly larger quantity of solution No. 2.

5. When a long series of tests is made consecutively, it is advisable to check the relation between volume and weight of nitrogen found in 3. by a second determination, using 10 c.c. of solution No. 1.

6. Instead of the mode of calculation given in 4., which is based simply upon a comparison of the nitrogen to be determined with a known quantity under identical conditions, the volume of the evolved gas may of course be measured and the weight calculated from it; in that case, regard must be had to the barometric pressure, the temperature, and the degree of moisture, as well as to the circumstance that a small quantity of nitrogen, dependent on the temperature, remains dissolved in the decomposing liquid. These calculations may be avoided by making use of E. Dietrich's * Tables on pp. 562–564.

7. Knop uses, as normal solution, an aqueous solution of sal-ammoniac containing 10 grams of pure dry chloride of ammonium in 2089·4 c.c. Each c.c. of such a solution corresponds with 1 c.c. of dry nitrogen gas at 0° and 760 mm. pressure.

In § 302, γ, the description of the azotimetric method for determining the ammonia in soils is relegated to azotimetry in manure analysis. It is therefore necessary to mention here the special details required when applying the method to the analysis of soils. They are as follows:

1. Knop now uses,† instead of his original form of decomposing vessel having a lead cover,‡ a wide-necked flask, divided internally by a vertical glass partition into two unequal parts. This replaces the vessel *a* in Fig. 131 (this vol. p. 560), but has the same appendage *b* and glass tap.

2. As the one chamber must be large enough to contain 100 grams of soil and also 125 c.c. of liquid, the vessel will be so large that it cannot be immersed in the same cooling cylinder with the U-tube, but must be cooled in a separate vessel, care being taken that the temperature at the beginning and end remains the same.

3. A quantity of fine earth corresponding with 100 grams of earth dried at 125°, is placed in the large chamber of the decomposing vessel and mixed with 125 c.c. of a clear saturated solution of borax; § 25 c.c. of the hypobromite is introduced into the smaller chamber as above, the stopper is placed in position, the upper glass vessel is connected with the U-tube, and both it and the decomposing vessel are surrounded with water in the cooling vessels. The whole is then allowed to remain for 20 minutes; the columns of water are adjusted to the proper level in the U-tube, and the hypobromite is gradually brought into contact with the soil by shaking moderately, the tap in *b* being open at first and then closed. This suffices for the complete decomposition of the ammonia. When the decomposing vessel has regained its original temperature, the nitrogen is measured; as the amount of the liquid in the vessel is not very small, the amount of nitrogen absorbed by it must not be neglected

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* Zeitschr. f. anal. Chem. 5, 38–40.

† *Ibid.* 25, 304.

‡ Chem. Centralbl. 1860, 251.

§ The object of using borax solution is to avoid the errors due to the contraction which usually takes place when soils are agitated with strongly alkaline liquids.

in accurate experiments. DIETRICH [*] has pointed out, however, the difficulty of estimating this factor with accuracy.

4. According to A. BAUMANN,[†] incorrect results are obtained by treating the soil as in 3. He proposes, as had already been done by DIETRICH (*loc. cit.*), to submit, not the soil, but its hydrochloric extract, to the azotimetric test. According to W. KNOP [‡] the inaccurate results obtained by others in direct azotimetric estimation of soils are due to their having employed a hypobromite which contained too much alkali. To avoid the error due to this cause, he recommends, in his most recent description of the method for preparing the decomposing liquid, to simply pour on to the earth mixed with borax solution a filtered solution of hypobromite of lime (200 c.c. of water, hydrate of lime in excess, and 15 c.c. bromine), or at the most to add a small quantity of hydrate of soda.[§]

III. SUBSTANCES CONTAINING NITROGEN IN ORGANIC COMBINATION.

The nitrogen in organic compounds can be determined by the methods described in § 183 to § 188 (this vol. pp. 36 to 56).[‖] As a rule, until lately, PELIGOT's modification of VARRENTRAPP and WILL's process (§ 187) was almost exclusively employed. In 1883, however, J. KJELDAHL published a method of estimating nitrogen founded upon an entirely new principle, and this rapidly obtained recognition, so that it would appear as though the VARRENTRAPP and WILL process would be gradually driven out of the field by that of KJELDAHL—at all events, for manure analysis.[¶]

Before explaining KJELDAHL's process, the description in this vol. p. 55 may be supplemented in a few points concerning the mode of carrying out PELIGOT's modification of VARRENTRAPP and WILL's method on a scale suitable for manufacturing works.

a. Modified VARRENTRAPP *and* WILL *Method.*

§ 323.

1. Both THIBAULT and P. WAGNER [**] recommend igniting the substance with soda lime in a current of hydrogen in a wrought-iron tube open at both ends (Fig. 132). This is 95 cm. long and 17 mm. wide, extending beyond the combustion furnace 17 cm. in front and 25 cm. behind, and

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[*] Zeitschr. f. anal. Chem. 5, 44.

[†] Landwirthschaftl. Versuchst. 1886, p. 247.

[‡] Zeitschr. f. anal. Chem. 26, pt. 1.

[§] As the treatises of A. BAUMANN and W. KNOP only came under the author's notice when correcting the proofs of this Appendix, it was merely possible to include their chief features in the text. All those, therefore, who are occupied with the estimation of ammonia in soils are advised to thoroughly study both treatises.

[‖] Since § 185 was written a whole series of investigations has appeared (for which see the Zeitschr. f. anal. Chem.) on DUMAS' method of nitrogen determination. KREUSLER (Landwirthsch. Versuchsst. 31, 207; Zeitschr. f. anal. Chem. 24, 438) has published a treatise dealing with all the details of the method as well as giving a modified form of the process which yields the most trustworthy results.

[¶] See MÄRCKER and HEFFTER, HOLLRUNG and MORGEN (Chemikerzeit. 8, 432; Zeitschr. f. anal. Chem. 23, 553); E. SCHULZE and BOSSHARDT (*ibid.* 24, 199); TH. PFEIFFER and F. LEHMANN, *ibid.* 24, 388).

[**] Chemiker-Zeitung, 8, 650; Zeitschr. f. anal. Chem. 23, 557.

resting in a trough of sheet-iron. The ends are closed by caoutchouc stoppers. In the front portion of the tube, and about 15 cm. from the mouth, is placed a layer of soda lime some 12 cm. in length, granulated but *not sintered;* this, which is kept in position between an asbestos plug in front and a roll of iron wire gauze behind, is sufficient for about 100 combustions. To fill the tube, the substance is first mixed with powdered soda lime in a mortar, and by the aid of a copper capsule *h*, the substance is transferred to a sheet-iron trough *i*, some 31 cm. long, provided with a turned down piece of plate at the back. To collect any portions which may be spilt, the iron trough is laid in a copper trough *k*, 3½ cm. wide. After covering the mixture in *i* with the soda lime used for washing out the mortar, &c., it is inserted in the iron tube and pushed home by the wire *e* which is left in with it; the tube is closed by the caoutchouc stopper, the receiver is attached, and a slow current of hydrogen * (which must be maintained throughout the whole of the combustion) is passed through the apparatus. The soda lime is first heated to redness, and then, gradually, the mixture of the organic substance with the soda lime, from front to back. The termination of the combustion is ascertained by stopping the supply of hydrogen, and observing whether the height of the acid in the receiver changes or not. In the latter case, and if no more gas bubbles are evolved, the burners are extinguished, the receiver changed, the iron trough and wire are withdrawn by a hooked wire *n*, as soon as the tube is no longer red hot, and the tube is then re-charged with a freshly filled trough, and another combustion begun.

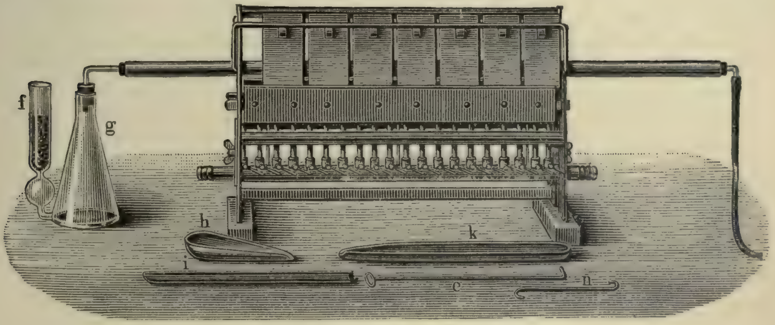

Fig. 132.

P. Wagner recommends the apparatus *gf* as a receiver. The acid is poured in at *f* which is partly filled with glass-wool. The escaping hydrogen having to pass through the glass-wool moistened with acid, gives up to the acid the last trace of ammonia. P. Wagner titrates back by introducing rosolic acid into *g*, adding titrated soda solution until there is a red coloration, then transfers the liquid into a porcelain dish, pours it again into the receiver through the tube *f*, thence back again into the porcelain basin, and completes the titration. The receiver is rinsed out a second and third time with the titrated liquid; adding lastly, when necessary, more soda lye until the final reaction is persistent. Should the final reaction not be sufficiently distinct owing to coloration by empyreumatic products, a few drops of acid is added to the titrated liquid, which is then evaporated to dryness in a water bath: the residue is rinsed into the azotimeter with 10 c.c. of water and the nitrogen determined by the aid of the latter (this vol. p. 599). P. WAGNER points out that if the method prescribed is followed, the acid only very rarely exhibits any coloration, and that very trustworthy results can be got even with such substances as blood meal and leather meal,* although they can only be obtained with difficulty by combustion in a glass tube without a current of hydrogen.

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* G. Loges (Chemiker-Zeit. 8, 1741; Zeitschr. f. anal. Chem. 24, 449) uses, instead of hydrogen, a current of coal gas freed from ammonia by passing it through a vertical tube filled with glass beads moistened with dilute sulphuric acid (1 pt. concentrated sulphuric acid to 3 pts. water).

2. If the fine state of division of the organic substance requisite for carrying out VARRENTRAPP and WILL'S process cannot be obtained, or only with great loss of time, the substance (for example, horn shavings, wool, &c.) must be treated with concentrated sulphuric acid, warming if necessary, until a clear thickish liquid is obtained. After sufficient action, the excess of sulphuric acid is carefully neutralised with finely powdered carbonate of lime and the dry powder thus obtained is mixed with soda lime (GRANDEAU,† KRAUCH‡). GRETE,§ who essentially recommends this treatment, neutralises the sulphuric acid with soda lime. It should be pointed out that sulphate of ammonia may be formed by the action of sulphuric acid on nitrogenous organic substances if heated (see KJELDAHL'S method below), so that in such cases care must be taken that in adding the soda lime, there is no loss of ammonia. If it is advisable to take a large quantity of the substance under examination in order to obtain a correct average sample, the dry powder obtained after treatment with sulphuric acid and carbonate of lime is weighed and an aliquot part of it employed for the combustion with soda lime.

b. KJELDAHL'S *Method.*||

§ 324.

KJELDAHL'S method is founded upon the fact, previously unknown, that the nitrogen in nitrogenous organic matter is converted into ammonia when the substance is thoroughly heated for a short time with abundance of sulphuric acid to a temperature approaching the boiling point of the acid, and the solution thus obtained is oxidised with dry permanganate of potassa. After super-saturating with caustic soda or potassa, the ammonia can be distilled off and determined by the usual methods.

DAFERT,¶ who has investigated the reactions occurring in this interesting process, states them to be as follows:

1. The sulphuric acid withdraws from the organic matter the elements of water, with formation of the latter.

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* Compare herewith KREUSLER'S investigations (Landwirthschaftl. Versuchsstat. 31, 248; Zeitschr. f. anal. Chem. 24, 446) which are generally confirmatory of WAGNER'S.

† His Handbuch für agriculturchem. Analysen, German edition, p. 18.

‡ Chemiker-Zeitung, 5, 703.

§ Zeitschr. f. anal. Chem. 18, 486.

|| Zeitschr. f. anal. Chem. 22, 366. As this method is of great importance for estimating nitrogen, not only in manures but also in organic substances, and could not be described earlier in the present work, it is here given in full detail.

¶ Zeitschr. f. anal. Chem. 24, 455.

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2. The sulphurous acid produced by heating the sulphuric acid with the carbonised mass exerts a reducing action on the nitrogenous substances.

3. By the powerful oxidising effect of the permanganate of potassa, any stable nitrogenous decomposition products which may have been produced are converted into ammoniacal compounds.

The reaction 2. is the principal and general one, that mentioned under 3. can only be considered as completing it under certain conditions.

According to Von Asbóth,* hydrogen is also disengaged by the action of sulphuric acid on organic substances containing this element, and this effects the conversion of the nitrogen into ammonia. He bases this opinion upon the fact that the whole of the nitrogen is obtained as ammonia only when there is no scarcity of substances containing hydrogen.

Kjeldahl's method, after being made public, was very quickly and repeatedly tested and has, as already mentioned, on account of the ease and rapidity with which it can be carried out, from its extended application, and from the trustworthiness of the results, as well as its small cost, gained universal recognition both in its original form and in its manifold modifications. It is divided as already stated into two operations, namely, *a.* decomposition of the organic matter and conversion of the nitrogen into ammonia, *b.* the estimation of the ammonia in the solution obtained by *a.*

In the following, the method will be first described in its original form, and then the modifications proposed and adopted.

a. KJELDAHL'S *Original Process.*

§ 325.

About 0·7 gram of substance, in the case of those containing 1–2 per cent. of nitrogen, or 0·25 gram when they contain about 5 per cent.† is weighed out. The substance need be only in such a state of division as to enable a true average sample to be obtained, and weighing may be performed in the small flask used for dissolving it; this is of about 100 c.c. capacity, made of good, refractory glass, with a rather long and narrow neck. If the substance is liquid, a quantity corresponding with the suitable amount of dry matter is taken, and the solvent evaporated (where loss of ammonia is not thereby to be feared‡) in a drying cupboard, or on a water-bath in a current of air freed from ammonia. 10 c.c. of pure concentrated sulphuric acid, to which, in order to compensate for the water in it, a little fuming sulphuric acid, or preferably phosphoric anhydride has been added,§ is now introduced into the flask, and the latter, inclined at an angle during the reaction, is heated over wire gauze or a small flame. A good draught is requisite for the operation, as fumes of sulphuric acid and sulphurous acid are plentifully disengaged. As a rule, the contents of the flask are at first dark and tarry. By continuing to heat until the acid is nearly at its boiling point, when occasional "bumpings" occur in the liquid from time to time, a brisk reaction sets in with evolution of gas, during which the substance completely dissolves. When the evolution of gas ceases, the condensed vapours of sulphuric acid wash the sides of the flask clean again, and any carbonised particles which have splashed up are carried back into the liquid. After a couple of hours or so of continued heating, the solution appears clear and is pale brown. In the case of many substances, however, such as albuminous substances and their derivatives, it is not necessary to carry the action so far as this, the object being accomplished by one or two hours' heating, even if the mixture still remains black; with substances, however, which offer greater resistance to the conversion of their nitrogen into ammonia it is best to continue the heating until decolorisation takes place, which is most easily effected if phosphoric anhydride is used.

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* Chem. Centralbl. 1886, 165; Zeitschr. f. anal. Chem. 25, 575.

† When the substance is still richer in nitrogen, Kjeldahl recommends, instead of reducing the quantity, to take an amount equal to four times that which is requisite, making up the acid solution to 100 cc., and taking 25 cc. for estimating the ammonia.

‡ Urine should not be evaporated, Pflüger and Bohland (Zeitschr. f. anal. Chem. 24, 636).

§ The sulphuric acid, or mixed acids, must be free from ammonia and carefully preserved from contamination with it. To make sure, 0·5 gram of pure sugar is treated with 10 c.c. of the acid precisely as described in the text, oxidising with permanganate of potassa, and distilling from caustic soda or potassa. If any

Ordinarily, by treatment with sulphuric acid, or a mixture of it with phosphoric anhydride, the greater part of the nitrogen, and in many substances, as for instance, urine, gluten-proteid substances, &c., the whole, is at once converted into ammonia, but with other albuminoid substances and the majority of those belonging to the series of fatty compounds, only 90 to 95 per cent. is thus converted, and in the case of many alkaloids (quinine, morphine) only 25 to 40 per cent. of the nitrogen is changed into ammonia.

When the action of the acid is at an end, the lamp is removed, and powdered permanganate of potassa is added to the liquid in small portions at a time in rapid succession—preferably in the form of a continuous shower of dust.* The reaction is very brisk and is accompanied by the evolution of greenish vapours and strong detonations; very often, small flames also flash out. No ammonia is lost during the operation.

The liquid, usually dark at first, quickly becomes paler by the action of the permanganate of potassa, then colourless, and on further addition of the salt dark green, or, when phosphoric acid is employed, blue green from the formation of salts of peroxide of manganese. When this coloration commences, the oxidation is complete and the liquid is left to cool.

The cooled acid solution is diluted by being poured into the distilling flask containing water, rinsing out well also with water; on adding the water, the green colour of the liquid changes to brown. The distilling flask has a capacity of about 750 c.c., and the tube fitted to it is bent sharply upwards at an angle, and connected with a condenser; KJELDAHL employs for this purpose a spiral tube whose lower end leads

ammonia is obtained in this way, the amount must be deducted from the result of the estimation (see the calculation).

* KJELDAHL recommends for producing this a wide glass tube with a narrow mouthpiece, such as the broken off upper part of a condenser tube, in the interior of which, at the bottom, a piece of fine wire gauze is fixed. By shaking or gently tapping the wide tube filled with dry rather finely powdered permanganate this falls through the gauze.

to an absorption apparatus. The latter consists of a 250 c.c. Erlenmeyer flask with a caoutchouc stopper pierced with two holes. The lower straight portion of the condenser tube passes through one of these down to the middle of the flask, without dipping into the acid, and through the other passes a glass tube bent at right angles and open to the air.

30 c.c. of N/20 sulphuric acid is placed in the absorption flask, the stopper of the distilling flask is taken out, a few zinc clippings are thrown into the liquid to prevent "bumping," and then immediately 40 c.c. of caustic soda of sp. gr. 1·3 is poured in; it is closed again without delay, and the liquid, which is now alkaline, is heated until all the ammonia has passed over, as is usually the case when about half the liquid has distilled.

The ammonia in the receiver can now be determined by any convenient method. **Kjeldahl** gives the preference to an older volumetric process now little used, founded upon a reaction by which, on adding an acid to a mixture of iodate and iodide of potassium, an amount of iodine is liberated equivalent to that of the acid, and can be titrated by means of hyposulphite of soda. To carry out this process, a few crystals of iodide of potassium are dissolved in the still acid liquid in the absorption flask, well made thin starch paste is added in sufficient quantity, followed by a few drops of a solution containing 4 per cent. of iodate of potassa, and finally a titrated solution of hyposulphite of soda (which is about equal to the N/20 acid) until the liquid is decolorised. As such a dilute solution of hyposulphite of soda is not very stable, it must be standardised afresh for every series of tests, which is done either as in § 146, by iodine, or as above, using a titrated acid.

As already mentioned, **Kjeldahl** checks his results by repeating the test with 0·5 gram of pure sugar, using identical quantities of acid and the other reagents so as to eliminate errors due to the presence of nitrogen in them. If 30 c.c. of N/20 sulphuric acid require 30 c.c. of hyposulphite of soda solution, but only 29·8 c.c. in the control experiment, then the latter figure must be used in calculating the analysis.

This calculation is very simple. The amount in cubic centimetres of N/20 solution of hyposulphite of soda, corresponding with the neutralised acid, is multiplied by 7·02 (half the equivalent of nitrogen), and the number thus obtained, when divided by the number of centigrams of substance taken, gives the percentage of nitrogen in the latter. **Kjeldahl** gives as example an estimation of nitrogen in barley.

0·645 gram of barley was treated as prescribed, 30 cc. of N/20 sulphuric acid being required. The relation found between this and the N/20 solution of hyposulphite of soda in the control experiment was 30 : 29·8. Titrating back required 14·5 c.c. of hyposulphite of soda solution:

$$29{\cdot}8 - 14{\cdot}5 = 15{\cdot}3\,;\ \frac{15{\cdot}3 \times 7{\cdot}02}{64{\cdot}5} = 1{\cdot}66 \text{ per cent. of Nitrogen.}$$

β. *Modifications of* KJELDAHL'S *Method.*

§ 326.

As can be seen from what has been stated in § 325, **Kjeldahl's** method was first brought out in a form which had been worked out with the greatest care, and the test analyses communicated by him likewise leave hardly anything to be desired on the score of accuracy. Nevertheless almost all the chemists who have occupied themselves with the testing and use of this method—and their number, as may be seen from the references in the footnote,* is large—have made and recommended modifications.

Many of them are only slight alterations. WILFARTH's modification, however, is of more importance, as are also those of v. ASBÓTH and JODLBAUER in connection with the estimation of nitrogen in nitrates. The slighter modifications will first be described, then WILFARTH's process, and finally the modifications introduced by v. ASBÓTH and JODLBAUER.

As nearly all the chemists named in the footnote titrate the excess of acid in the ammonia estimation, by the ordinary acidimetric method, with baryta water or caustic soda—using litmus or other indicator—without mentioning the method employed by KJELDAHL based upon the separation of iodine, they use larger quantities of substance (1–1·5 grams), larger flasks for the heating (from 150 to 250 c.c. capacity), and 20 c.c. instead of 10 c.c. of the acid mixture. With reference to the latter, many discard fuming sulphuric acid (which often contains nitric acid) and employ a solution of 200 grams of anhydrous phosphoric acid in 1 litre of pure concentrated sulphuric acid, whilst others use a mixture of equal volumes of concentrated and fuming sulphuric acid; others again prefer this mixture or a similar one containing 4 vols. of concentrated and 1 vol. of fuming sulphuric acid, to which is added 100 grams of phosphoric anhydride per litre of the mixture. BRUNNEMANN and SEYFERT mix the substance with 2 grams of phosphoric anhydride, then heat with 5 c.c. of a mixture of 4 vols. of concentrated and 1 vol. of fuming sulphuric acid until the brisk evolution of gas has subsided, continuing the heating after adding 15 c.c. more of the acid mixture.

Other alterations consist in changing the manner, intensity and duration of heating. All are, however, agreed that the safest way is to allow the action to continue until the solution has become the colour of Rhine wine, or appears reddish or colourless. HEFFTER, HOLLRUNG and MORGEN, as also KREUSLER, have described special stoves for heating many flasks at a time. KREUSLER placed over the flask a cylindrical glass vessel open above and below to lessen the evolution of acid vapours. ULSCH uses glass balls with stems.

CZECZETKA employs a solution of permanganate of potassa in concentrated sulphuric acid for oxidising, instead of the powdered dry salt.

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* HEFFTER, HOLLRUNG and MORGEN (Chemikerzeit. 8, 432; Zeitschr. f. anal. Chem. 23, 553); PETRI and TH. LEHMANN (Zeitschr. f. physiolog. Chem. 8, 200; Zeitschr. f. anal. Chem. 23, 596); E. BOSSHARD (Zeitschr. f. anal. Chem. 24, 199); E. PFLÜGER and K. BOHLAND (Archiv d. gesammte Physiolog. 35, 454, and 36, 102; Zeitschr. f. anal. Chem. 24, 299 and 635); TH. PFEIFFER and F. LEHMANN (Zeitschr. f. anal. Chem. 24, 388); KREUSLER (*ibid.* 24, 393 and 453; Landwirthschaftl. Versuchsstat, 31, 269); C. ARNOLD (Archiv. d. Pharm. [iii.], 23, 177; Zeitschr. f. anal. Chem. 24, 454; Chem. Centralbl. 1886, 337); F. W. DAFERT (Zeitschr. f. anal. Chem. 24, 454); H. WILFARTH (Chem. Centralbl. [iii.], 16, 17 and 113; Zeitschr, f. anal. Chem. 24, 455); BALCKE (Wochenschr. f. Brauerei, I. No. 11); P. KULISCH (Zeitschr. f. anal, Chem. 25, 149); RINDELL and HANNIN (*ibid.* 25, 155); CZECZETKA (Monatshefte f. Chem. 6, 63; Zeitschr. f. anal. Chem. 25, 252); A. V. ASBÓTH (Chem. Centralbl. 1886, 161); ULSCH (*ibid.* 375); M. JODLBAUER (*ibid.* 433); BRUNNEMANN and SEYFERT (Chemikerzeit. 8, 1820); R. WARINGTON (Chem. News, 52, 162; Zeitschr. f. anal. Chem. 25, 427).

A 500–750 c.c. flask is sufficient for the distillation, even when a larger quantity of the substance and 20 c.c. of acid mixture are taken. The quantity of liquid to be distilled is about 200 to 250 c.c. according to the amount of water used in dilution. The alkali solution—preferably potassa which is less likely than soda to cause "bumping" during boiling—is added to the cold diluted liquid, first in quantity sufficient to nearly neutralise the acid, to which, after it has been cooled, more of the alkali solution is added until it is in sufficient, but not too great, excess. When zinc cuttings are used, a large excess of alkali must be particularly avoided as if the evolution of hydrogen is too brisk it is difficult to prevent drops of the alkali from being carried over, even when a safety apparatus is provided, of which several have been proposed. Should the lye contain nitric acid, the nitrogen of this, when zinc is used, is converted into ammonia. To prevent "bumping," the passage of a gentle current of steam or air has been recommended. Of course, the form of distilling apparatus and receiver admits of manifold modifications. The use of a bulb, partly filled with pieces of glass, in the upward inclined portion of the tube leading from the distilling vessel to the condenser, is always advisable. The apparatus described in Vol. I. p. 179, and shown in Fig. 78, is also suitable for distillation, as well as that, in so far as the receiver is concerned, shown in this vol. p. 558, Fig. 130.

If, as recommended by most of the chemists mentioned above, a larger quantity of substance be taken, a stronger acid than the N/20 acid used by KJELDAHL must be employed, in fact normal, N/2, or N/10 acid, according to circumstances.

PFLÜGER and BOHLAND, who have retained and recommend titration based upon the iodine method used by KJELDAHL, draw attention to the fact that the last small portions of free acid require time to decompose the mixture of iodide of potassium and iodate of potassa, particularly in the case of very dilute solutions. For complete decomposition, about 24 hours are required, but at the end of the first two hours the error only amounts to 0·1 to 0·2 c.c. of N/10 solution of hyposulphite of soda.

In titrating the excess of acid by ordinary acidimetric methods, many give baryta water the preference over potassa or soda solution. As indicators, SCHLÖSING's preparation of litmus * (this vol. footnote, p. 533), methyl-orange, and phenacetolin (THOMSON †) are especially to be recommended.

WILFARTH's modification is founded upon the fact that the addition of metallic oxides hastens the action of the acid mixture on the organic matter; the most suitable are oxide of copper, and especially mercuric oxide prepared in the wet way, as this oxide when made by the dry method is apt to contain nitric acid. WILFARTH's modification, which has proved trustworthy in every respect, is carried out as follows:

About 1 gram of the nitrogenous substance (2 to 3 grams may be taken if it is poor in nitrogen) is heated with 20 c.c. of an acid mixture consisting of 3/5 vol. of pure concentrated sulphuric acid and 2/5 vol. of fuming sulphuric acid, with the addition of about 0·7 gram of mercuric oxide prepared in the wet way (or a corresponding amount either of mercuric sulphate or of metallic mercury), the flask, which should be of good potash glass, being heated on a wire gauze or over a naked flame,

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* Compare RINDELL and HANNIN, Zeitschr. f. anal. Chem. 25, 155.

† *Ibid.* 24, 225.

very moderately at first, then rather more strongly, and finally to gentle boiling. If heating be continued until the liquid is quite colourless, oxidation by permanganate of potassa is unnecessary, but if it is desired to save time the liquid is heated only until it is of the colour of light Rhine wine, and is then oxidised with permanganate of potassa. After it has been diluted and made alkaline by caustic potassa as described above, an amount of sulphide of potassium solution (containing 40 grams of *Kalium sulfuratum* per litre) more than corresponding with the mercury used is added, so as to throw down the mercury as sulphide. In order to approximately ascertain the amount of sulphide of potassium solution required, 0·5 gram of mercuric oxide is dissolved in dilute sulphuric acid, and an experiment made to see how much of the sulphide of potassium solution is necessary for its precipitation. It is advisable to add a considerable excess of sulphide of potassium to make sure that the mercuro-ammonium compounds have been completely decomposed. It is only after twice or three times the requisite amount has been added that the smell of sulphuretted hydrogen is perceptible, but this does not affect the accuracy of the results. "Bumping" does not occur when the liquid holds sulphide of mercury in suspension, at least if solution of potassa is used; if necessary, a little zinc may of course be added.

WILFARTH's method also has been modified, KULISCH recommending an acid mixture of equal volumes of concentrated and fuming acid, containing 100 grams of phosphoric anhydride per litre. He only obtained absolutely correct results with the substances (wine yeast, and must extract) examined by him when the heating was continued until the liquid was decolorised, and subsequently oxidising with permanganate of potassa. KULISCH recommends adding a small quantity of metallic mercury. ARNOLD takes 0·5 gram of sulphate of copper with 1 gram of metallic mercury, and ULSCH 0·05 gram of oxide of copper with 5 drops (no more) of a solution of perchloride of platinum containing 0·04 gram of platinum in 1 c.c.

Should the nitrogen be present in the form of nitric acid, neither KJELDAHL's original method nor WILFARTH's modification of it yields good results. The object may, however, be obtained by making certain additions; according to v. ASBÓTH (*loc. cit.*) the purpose is fairly well fulfilled by the addition of benzoic acid. He recommends the employment of 1·75 gram of benzoic acid to 0·5 gram of saltpetre, finally decomposing the very stable benzoic acid by long-continued heating with permanganate of potassa. If the nitrogen is present as oxide, or in the form of cyanogen, v. ASBÓTH adds 1 gram of sugar; for the metallic addition, he uses 0·5 gram of sulphate of copper. The distillation is effected after adding caustic soda solution containing Rochelle salt (350 grams of Rochelle salt and 300 grams of hydrate of soda dissolved in 1 litre of water) so as to keep the oxides of copper and manganese in solution.

According to JODLBAUER (*loc. cit.*) the addition of benzoic acid when nitrates are present does not with certainty yield sufficiently accurate results, but they are quite satisfactory when 0·2 to 0·5 gram of nitrate of potassa (or the corresponding amount of another nitrate) is treated with 20 c.c. of concentrated sulphuric acid and 2·5 c.c. of phenolsulphonic acid (prepared by dissolving 50 grams of phenol in concentrated sulphuric acid to make 100 c.c.), with the addition of 2 to 3 grams of zinc dust and 5 drops of platinum chloride solution containing 0·04 gram of platinum in 1 c.c. After heating for about four hours, the liquid is colourless and ready for further treatment and distillation. If a mixture of sulphuric acid and phosphoric anhydride is used, two hours' heating is sufficient, but the decomposing flask is strongly attacked and in a short time becomes unusable.

F. Analysis of Manures containing two or more Manurial Substances.

In order to afford some guidance as to the choice of methods suitable for all cases, a general process is first given which may be used not only for stable manure, but for nearly all kinds of manures, subsequently the methods which are especially adapted for commercial manures are considered.

I. Usual Mode of Procedure.

§ 327.

The manure is mixed uniformly by chopping and grinding, and the several portions required for the various estimations are then weighed out successively.*

1. Determination of the Water.

10 grams are dried at 110°, and the loss of weight determined (§ 29). (It is seldom necessary to make a correction for the carbonate of ammonia which escapes with the water.†)

2. Total Amount of fixed Constituents.

A weighed portion of the residue left in 1 is incinerated at a gentle heat in a platinum dish (this vol. pp. 498–499), or in a large platinum crucible placed in an inclined position; the ash is moistened with a solution of carbonate of ammonia, dried, ignited gently, and weighed.

3. Constituents soluble in Water, and insoluble in Water.

10 grams of the fresh manure is digested with about 300 c.c. of water, collected on a weighed filter (§ 50), washed, dried at 110°, and weighed. In this way, the total weight of the substances insoluble in water is found, and the difference—after deducting the water found in 1—gives the amount of the soluble constituents. The insoluble residue is now incinerated, treated with carbonate of ammonia, as in 2, and weighed; this gives the total amount of the fixed constituents contained in the insoluble part, and the difference the total amount of those contained in the soluble part.

4. Fixed Constituents singly.

A larger portion of the manure is dried, and treated by one of the methods given for the preparation and analysis of the ashes of plants.

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* If this has to be done, the operation is the same as in the determination of water in guano (§ 331, 1).

† Accurate instructions for obtaining a true average sample of stable manure are given in E. Wolff's "Anleitung zur chem. Untersuch. landwirthschaftl. wichtiger Stoffe" (Berlin, Wiegandt, Hempel und Parey), 3rd edition, p. 115.

5. Total Carbon.

A portion of the residue obtained in 1 is subjected to an elemental analysis, and as manures may contain chlorine and sulphur compounds it is preferable to make a combustion with chromate of lead (§ 176).

As regards the content of nitrogen, what has been said in § 183, and, for the inorganic substances, that in § 191 must be borne in mind. If the dried manure contains carbonates, the carbonic acid must be determined in a separate portion, and by deducting the amount thus obtained from that found in the elementary analysis, the difference will give the amount derived from the carbon of the organic matter. The method given in this vol. p. 323—namely, oxidation of the organic matter by chromic acid with addition of sulphuric acid—may also occasionally be employed with good results, namely, when no chlorine compounds are present.* In presence of carbonates, the properly diluted sulphuric acid is first allowed to act alone until all the carbonic acid is evolved, before adding the chromic acid and connecting the decomposing flask with the absorption apparatus.

6. Sulphur Compounds.

If a manure contains unoxidised sulphur, as, for example, is usually the case with that derived from the sewers of towns, the total amount of sulphur is determined in a sample by the method given for soil analyses (§ 303, *b*); a second portion is heated with dilute hydrochloric acid, repeatedly if necessary, filtered, and the sulphuric acid estimated in the filtrate; this was present as such in the manure, the unoxidised sulphur being represented by the difference.

7. Total Nitrogen.

§ 328.

If a manure, as is frequently the case, contains the nitrogen as nitric acid, ammonia, and in organic combination, then, without doubt, DUMAS' method (§ 185) is suitable for obtaining the total nitrogen at one operation. KJELDAHL'S method (§ 324 to 326) and that of VARRENTRAPP and WILL (§ 186 and 187), on the other hand, when any considerable amount of nitric acid is present, cannot be used in their original form, but the modifications hereafter described must be employed.

a. Preparatory Treatment.

When the manure is damp, not homogeneous, and gives off ammonia on drying, a weighed quantity of the manure, about 10 grams, is moistened with a dilute solution of oxalic acid so that the whole remains quite neutral or only slightly acid, and after being dried at 50° and weighed, it is mixed uniformly, and portions of the dried substance are used for the nitrogen estimation.—If the manure is of a similar nature but does not give off ammonia on drying, it is treated in the same way, but without adding oxalic acid. If on the other hand it is dry, homogeneous, and finely powdered, it is, of course, fit for examination without any preparation.

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* See however in this connection this vol. p. 529, *β*.

b. The Analytical Process.

α. Dumas' *Method.*—The only objection that can be urged against this method, which is minutely described in § 185, and the general nature of which is also referred to in this vol. p. 566 in the footnote, is that it is too complicated for the examination of manures. It cannot, however, be omitted when the checking of other methods is in question. Instead of forcing the nitrogen into the measuring cylinder by carbonic acid, the Sprengel mercury pump is now often employed with the best results. Compare with this the work of Frankland and Armstrong,* Gibbs,† Pflüger,‡ Johnsohn and Jenkins,§ Dabney, jun., and von Herff.||

β. Jodlbauer's *Modification of* Kjeldahl's *Method* (this vol. p. 574).—As already mentioned, this also gives accurate results when the nitrogen is present as nitric acid.

γ. Varrentrapp *and* Will's *Method and its Modifications.*—If the amount of salts of nitric acid is only small, and that of the organic matter sufficiently large, then Varrentrapp and Will's method, in its original form (§ 186) or in Péligot's modification of it (§ 187) (see this vol. p. 50), is satisfactory. If, however, the amount of nitric acid is somewhat larger, then modifications suitable for the energetic reduction of the acid must be chosen. Such have been repeatedly proposed and as they have not as yet been described they will be considered now, although they have no longer the same importance as they had originally, owing to the introduction of the modified Kjeldahl process, which more easily and surely accomplishes the desired end.

The first modification of Varrentrapp and Will's method, here considered, is due to E. A. Grete,¶ who employed a mixture of soda lime and xanthogenic salts to convert the nitric acid into ammonia.—Ruffle** subsequently recommended a mixture of 2 equivalents of hydrate of soda, 1 of lime, and 1 of crystallised hyposulphite of soda. He filled the iron combustion tube, which is closed at the further end, as follows: 5 grams of the mixture was placed at the further end, then about 30 grams of the same ground up with 1 to 1·5 grams of the substance to be analysed, the latter having previously been thoroughly incorporated with about 1 gram of a mixture of equal parts of flowers of sulphur and powdered charcoal; then followed more soda-lime mixture, succeeded by about 18 grams of pure soda-lime, and finally a plug of asbestos, so placed as to leave still about 20 cm. of the tube empty. Ruffle's test analyses are satisfactory. In the analyses of artificial manures, it is sometimes necessary to bring the substance into intimate contact with hyposulphite of soda by evaporating it with a solution of the latter. A. Guyard (H. Tamm††) proposed heating to redness a mixture of the substance with soda-lime and dried acetate of soda. A. Goldberg‡‡ recommends a mixture of 100 parts of soda-lime, 100 parts of stannous sulphide, and 20 parts of sulphur; with this, approximate (about 0·3 to 1·0 per cent. too low) results were obtained in the case of saltpetre.

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* Zeitschr. f. anal. Chem. 8, 489.

† *Ibid.* 11, 206.

‡ *Ibid.* 18, 296.

§ *Ibid.* 21, 274.

|| *Ibid.* 25, 425.

¶ Ber. d. deutsch. chem. Gesell. 11, 1557; Zeitschr. f. anal. Chem. 18, 106.

** Journ. Chem. Soc. 1881, 87; Zeitschr. f. anal. Chem. 21, 412.

†† Chem. News, 45, 159; Zeitschr. f. anal. Chem. 21, 584.

‡‡ Zeitschr. f. anal. Chem. 23, 244.

The majority of these proposals were soon tested on different sides, and with very varying results. First as concerns Ruffle's process, Crispo,[*] Pellet,[†] and also Dabney, jun., and v. Herff[‡] obtained good results by its use; Fassbender,[§] on the other hand, as well as Arnold,[||] who effected the combustion in glass tubes and consequently used dehydrated hyposulphite of soda, arrived at much less satisfactory results. Shepherd[¶] obtained approximately accurate values when dealing with guanos containing small quantities of nitre, but they were too low in the case of saltpetre. G. König[**] says that the method gives correct results with natural Peruvian guanos, also when they contain nitrate, but they are too low in the case of artificial mixtures of guano and saltpetre; Rube[††] also obtained good results with manures, especially guano, and attributes the unfavourable results recorded by others to their not having strictly adhered to Ruffle's original method but having made alterations in it.

P. Wagner[‡‡] also obtained useful results with guanos containing nitre, by the following slightly modified process in which the subjoined mixtures were employed: I. 100 parts by weight of powdered soda-lime and 10 parts by weight of oxalic acid.—II. 100 grams of calcined gypsum with 6 c.c. of concentrated pure sulphuric acid (stored in tightly closed glass bottles). III. 100 parts by weight of hyposulphite of soda dried at 100° and intimately mixed, in a warmed mortar, with 100 parts of powdered and well-dried soda-lime, 8 parts of finely powdered wood charcoal, and 8 parts of flowers of sulphur (to be stored in a narrow-necked glass bottle closed by a caoutchouc stopper). The glass tube used for the operation is 40 cm. long and 8 mm. wide, fused up and rounded at one end, and is charged first with a layer of the mixture No. I., 5 cm. long; 1·5 gram of an intimate admixture of equal parts by weight of the guano under examination and of mixture No. II. is mixed with about 20 grams of No. III., then introduced into the tube without delay, and the latter is filled with granulated soda-lime, and plugged with asbestos. Any correction which may be requisite is ascertained by blank combustions.

J. König (*loc. cit.*) found that Grete's method yielded the same results as Ruffle's; on the other hand, Tamm's process found no defender, although C. Arnold[§§] and subsequently Houzeau[||||] attempted a combination of Ruffle's and Tamm's methods with success. In his latest publication, C. Arnold[¶¶] recommends heating 0·5 gram of substance (or 0·3 gram only if the substance contains more than 20 per cent. of nitrogen) with a mixture of 2 parts of dehydrated hyposulphite of soda to each 1 part of soda-lime and formate of soda (to which a little sugar is added when analysing nitrates of the heavy metals). The glass tube contains, at the further end, 5 cm. of the mixture just described, then the mixture containing the substance (12 to 15 cm.), followed by a 15 to 20 cm. layer of the finely powdered mixture, and finally 5 to 10 cm. of soda-lime. The heat during combustion should not be raised so as to sinter the mass and cause it to form a large channel, but must nevertheless be sufficient for the complete combustion of the substance. If this is not the case, and the acid in the receiver appears dark or turbid in consequence, the results are not trustworthy. Those obtained by Arnold with this process, from nitrates and nitro-compounds, are entirely satisfactory.

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[*] Neue Zeitschr. f. Rübenzuckerindustrie, 9, 162; Zeitschr. f. anal. Chem. 22, 434.

[†] Rev. d. ind. chim. et agr. 6, 605; Zeitschr. f. anal. Chem. 22, 434.

[‡] Amer. Chem. Jour. 6, 234; Zeitschr. f. anal. Chem. 25, 425.

[§] Rep. d. analyt. Chem. 2, 225; Zeitschr. f. anal. Chem. 22, 434.

[||] Arch. d. Pharm. [iii.], 20, 92; Zeitschr f. anal. Chem. 22, 435.

[¶] Chem. News, 47, 75; Zeitschr. f. anal. Chem. 22, 435.

[**] Rep. der anal. Chem. 3, 1; Zeitschr. f. anal. Chem. 22, 436.

[††] Zeitschr. f. anal. Chem. 23, 43.

[‡‡] Chemikerzeit. 8, 651; Zeitschr. f. anal. Chem. 23, 559.

[§§] Rep. der analyt. Chem. 2, 331; Zeitschr. f. anal. Chem. 22, 437.

[||||] Compt. rend. 100, 1445; Zeitschr. f. anal. Chem. 25, 424.

[¶¶] Rep. der analyt. Chem. 5, 41; Zeitschr. f. anal. Chem. 24, 451.

Finally it may be pointed out that the total nitrogen can be ascertained by adding together that existing as nitric acid (see below 8, β.) and the sum of the amounts present as ammonia and in the organic matter (see below 8, γ, *bb.* or *cc.*)

8. Nitrogen in its Different Forms of Combination.

§ 329.

a. As Ammonia Compounds.

The ammonia is most conveniently determined by distilling a weighed sample with water and calcined magnesia (Vol. I. p. 178, and this vol. p. 557). Should organic matter be present, the nitrogen of which may be thereby partly converted into ammonia, it is preferable to employ Schlösing's process based on the action of milk of lime in the cold (Vol. I. p. 179 *b*, and this vol. p. 531). If it is desired to estimate the ammonia volumetrically, this is best effected in a hydrochloric extract of the manure; compare § 322 (azotimetric estimation of ammonia in soils).

β. In the Form of Nitric Acid.

A sample of the manure is thoroughly extracted with water, the solution, after completely neutralising if acid, is concentrated by evaporation, made up to a known volume, and the nitric acid, and hence the nitrogen in it, determined, most conveniently by P. Wagner's modification of Schlösing's process (this vol. p. 554).

The *nitrometric method* (this vol. p. 447) can also be used with good results, and is especially recommended by many analysts.* In that case, the measured quantity of the aqueous solution, neutralised if necessary, is evaporated almost to dryness, a little sulphuric acid added to decompose any carbonates present, and the carbonic acid removed by gently warming; the liquid, which should measure 2 to 3 c.c. only, is placed in the nitrometer, and the funnel of the latter is rinsed out twice with concentrated sulphuric acid. Shepherd (*loc. cit.*) places the liquid, which together with the washings should not exceed 5 c.c., at once into the nitrometer, adds to the cold liquid twice its volume of concentrated sulphuric acid, mixing it with the aqueous liquid by gentle agitation, and allowing any carbonic acid evolved to escape by opening the tap for a moment; finally it is shaken vigorously to disengage the nitric oxide.

With manures which have an acid reaction, all direct evaporation of the aqueous extract must of course, as already mentioned, be avoided, otherwise there will be a loss of nitric acid ; to make a direct determination of this nitrometrically, a weighed, and not too small, sample is extracted with warm water in such a manner that whilst the residue is exhausted, the solution is as concentrated as possible ; it is then made up to a known volume, and 5 c.c. taken for the nitrometric examination (YARDLEY, *loc cit.*).

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* See Shepherd (Chem. News, 47, 76; Zeitschr. f. anal. Chem. 25, 270); Yardley (Chem. News, 47, 92; Zeitschr. f. anal. Chem. 25, 448).

γ. *In Organic Combination.*

aa. By deducting from the total nitrogen found by § 328 the nitrogen present as ammonia compounds (*α*) and that as nitric acid (*β*), the difference is the nitrogen in organic combination.

bb. According to O. REITMAIR,[*] when the manure contains nitrates, 3 c.c. of 50 per cent. sulphuric acid[†] is poured on to about 1 gram of the finely powdered sample in a flat capsule made of tin foil about 60 mm. in diameter and 20 mm. deep ; it is then stirred with a very short glass rod, and heated, first in a drying cupboard for 3 or 4 hours at 60 to 80°, and finally for one hour at 120–130°. A damp mass is now left in the dish from which the whole of the nitric acid (but no other nitrogen) has been removed. The amount of nitrogen in the residue can be determined either by KJELDAHL's or by VARRENTRAPP and WILL's method. If the former is used, the tin foil capsule and its contents are placed in the decomposing flask ; if the latter a powdered mixture of gypsum and marble is put into the capsule, the whole well stirred together, removed from the capsule and mixed with soda-lime in the usual manner. The tin foil capsule, sprinkled with lime and bent together, is also introduced, along with the glass stirrer, into the combustion tube.

If the nitrogen of the ammonia (8, *α*) is deducted from the total nitrogen determined in the residue left after driving off the nitric acid by one or other of the above methods, the difference gives the nitrogen present in the form of organic substances.

cc. The weighed substance, when it contains nitrates, is heated with a corresponding amount of ferrous sulphate and concentrated sulphuric acid ; after being completely freed in this way from nitric acid, the residue is dried, and the total nitrogen present as ammonia and in the form of organic compounds is determined by KJELDAHL's method (R. WARINGTON). The calculation is made as in γ, *bb.*

II. ANALYSIS OF COMMERCIAL MANURES.

1. Bone Preparations.

§ 330.

The bones of vertebrate animals in the dry state, contain about 70 per cent. of inorganic and 30 per cent. of organic matter. The former consists of basic phosphate of lime and small quantities of carbonate of lime, fluoride of calcium, and phosphate of magnesia ; the latter chiefly of cartilaginous substances and fat. The average proportion of nitrogen in the dried bones amounts to 4–5 per cent., the phosphoric acid to 27–30 per cent., and the fat to about 10 per cent. When boiled with water, as also on exposure to air, the proportion of nitrogen and fat decreases, whilst that of the phosphoric acid increases. The manurial value of bones depends on their state of division and their content of nitrogen and phosphoric acid. The presence of fat is rather prejudicial than otherwise. The following preparations of bone are met with in commerce :

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[*] Rep. der analyt. Chem. 5, 262 ; Zeitschr. f. anal. Chem. 25, 583.

[†] The employment of concentrated sulphuric acid as used by DREYFUS (Bull. de la Soc. Chim. de Paris, 40, 267 ; Zeitschr. f. anal. Chem. 23, 246), is not advisable as in presence of organic matter, as part of the nitrogen of the nitric acid may become converted into ammonia.

a. Bone-meal.

Bone-meal comes into commerce in three forms—namely, crude, steamed, and fermented. The crude should be guaranteed to contain 2·5 to 4·5 per cent. of nitrogen and 18 to 20 per cent. of phosphoric acid ; the steamed from 3 to 4·5 per cent. of nitrogen, and 20 to 21 per cent. of phosphoric acid ; and fermented bone-meal 4 per cent. of nitrogen and 20 per cent. of phosphoric acid. The analysis is generally confined to the estimations *a.*, *β.*, and *γ.*, occasionally also *δ.*

a. Moisture.—About 5 grams is dried at about 110°, in a light wide-mouthed glass (this vol. p. 539, fig. 128) and the loss in weight determined.

β. Ash, Sand, Phosphoric acid.—About 5 grams is heated, at first gently, but gradually more strongly with admission of air, until the ash becomes white ; this is moistened with carbonate of ammonia, dried, ignited gently, and *the ash* weighed. The latter after being gently boiled for some time with 15–20 c.c. of nitric acid, previously diluted with a little water, until all the soluble parts are dissolved, is diluted, filtered into a 500 c.c. measuring flask, and the insoluble residue washed, dried, ignited, weighed, and calculated as *sand.* When cold, the contents of the measuring flask are diluted up to the mark, mixed thoroughly, and the phosphoric acid (about 0·1 gram) determined in 50 c.c. according to § 309 or § 313 *ββ.*—If it is desired to ascertain the proportion of other substances (lime, magnesia, ferric oxide, &c.) contained in the ash, another measured portion of the nitric acid solution is treated as in § 287.

γ. Nitrogen.—As the nitrogen in the bone-meal is solely in the form of organic matter, it is sufficient to estimate it by the combustion of about 1 gram of substance with soda lime (§ 187 and § 323) or by KJELDAHL's method (§§ 325 and 326). In both processes, 20 c.c. of N/2 sulphuric acid are required.

δ. As, in fixing the manurial value of bone-meal, *the state of division* must be taken into account, this is determined by dividing 100 grams into four grades by the aid of three sieves of different gauges. STOHMANN * proposed the following sieves, I., II. and III. for this purpose : The No. I. has 11 meshes to the sq. millimetre ; No. II. 5 ; and No. III. 2·5. What remains on sieve III. is residue IV.

ε. If the proportion of fat has also to be determined, the residue obtained in *a* (after grinding down finer if necessary) is exhausted with carbon bisulphide or ether, in one of the forms of extraction apparatus suited for this purpose*; the solvent is then evaporated in a light, wide-necked weighing glass, the residue heated for some time at 100°, and the fat weighed.

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* WAGNER'S "Lehrbuch der Düngerfabrikation," pub. by Fr. Vieweg & Son, Brunswick, p. 187.

ζ. Carbonic acid may be estimated by one of the processes described in § 139, II.

b. *Animal Charcoal, or Bone Black.*

Animal charcoal ("char") is extensively employed in the manufacture of sugar for decolorizing, and for removing lime. When freshly prepared, it consists of a mixture of bone earth with 7·5–10·5 per cent. of carbon, but on being used it takes up lime, colouring matter, mucilage, &c., from which it is freed during the process of revivifying, by treating it with acids, fermentation, washing and igniting. When at last it is thoroughly used up, or "spent," it passes over to the manure manufactories, and is then usually employed for the preparation of superphosphate. As the animal charcoal is much altered and contaminated by the numerous operations through which it passes, the quality of that which comes into the market varies very considerably, and its value can only be estimated by analysis. This is one reason why bone black is so frequently analyzed, but there is another, for it is necessary to have analyses made of the animal charcoal which is to be submitted to the revivifying process after having been used in the sugar manufacture; as in order to ascertain the amount of hydrochloric acid necessary for its revivification, we have in each individual case to determine the quality of lime which is not combined with phosphoric acid (and usually present in the form of carbonate).

The method employed for the complete analysis of animal charcoal is fully described below, but it should be noted that as a rule the estimation of the phosphoric acid suffices to ascertain its manurial value.

1. About 5 grams is dried at 110°, and the *moisture* determined from the loss in weight.

2. About 5 grams is dissolved in the flask *a* of the apparatus figured on p. 234 of this vol., and the *carbonic acid* determined by the method there described. If the phosphoric acid alone has to be determined by the molybdic method in the filtrate, dilute nitric acid is employed as the solvent, otherwise hydrochloric acid is used. In order to be certain that all the soluble matters are dissolved, the acid must be allowed to act for 15 to 20 minutes at its boiling point.

3. The solution obtained in 2 is filtered through a filter which has been dried at 100° and weighed, and the residue is weighed, dried at 110°, and re-weighed; this gives the sum of the charcoal, any insoluble organic matter which may be present, and the mineral impurities insoluble in nitric acid or hydrochloric acid (sand and clay). The dried filter is then ignited with access of air, and this gives the *sand* and *clay* as residue, the amount of *charcoal* and insoluble *organic matter* being found by difference.

4. The filtrate obtained in 3 is made up to 500 c.c. and the *phosphoric acid* determined in 50 c.c. as in § 330, *a*. In other portions, the rest of the constituents, *iron*, *lime*, *magnesia*, *alkalies*, *and sulphuric acid* may be determined according to § 287.

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* See Zeitschr. f. anal. Chem. 12, 179; 14, 82; 17, 174, and 320; 18, 441; 21, 98; 22, 528; 24, 48; 25, 396; Rep. der analyt. Chem. 1886, p. 390.

5. Another weighed portion of the substance is dissolved in dilute nitric acid, diluted, and the *hydrochloric acid* which may possibly be present is determined.

6. For determining the *sulphide of calcium*, which is mostly present in quantities too small to allow of its precise estimation along with the carbonic acid (see 2), 10 grams of the bone-black is heated with dilute hydrochloric acid in a current of hydrogen, passing the gas, containing sulphuretted hydrogen, through brominated hydrochloric acid, estimating the sulphuric acid produced, and from this calculating the amount of sulphide of calcium, see this vol. p. 330.

7. For the estimation of *carbonate of lime*, or *carbonate* and *fre lime*, SCHEIBLER's process, described in Vol. I. p. 343, *g. a.*, is generally employed in works. The bone-black is previously dried and *ground as fine as possible.* The quantity taken is such as will yield a not too small amount of carbonic acid ; about 3 grams of bone-black may be considered as sufficient. SCHEIBLER fixed a normal weight for his apparatus, and in his treatise* gives tables for facilitating the calculation. If a bone-black contains hydrate of lime, the weighed sample is moistened in a porcelain dish with 10 to 20 drops of a solution of carbonate of ammonia, evaporated to dryness, the residue heated rather more strongly (but never to redness), and the contents of the dish transferred to the decomposing flask without loss.

With careful working, the results are very accurate and concordant, and many analyses can be made in a short space of time.

c. Bone-ash and

d. Precipitated phosphate of lime from bones.

This owes its value solely to the phosphoric acid present, which may be determined according to § 307–310, or by § 313 *ββ*.

e. Superphosphates manufactured from bone preparations.

If these are prepared from bone-black or bone-ash, only the phosphoric acid in its different conditions of solubility has to be considered in fixing their value, but if, on the other hand, they are made from bone-meal, then the nitrogen also has to be determined.

As regards the estimation of phosphoric acid, see § 311 to § 318, the estimation of nitrogen is carried out as in the case of bone-meal § 330 *a*, *γ*).

2. Guano (Peruvian guano)

§ 331.

a. Crude guano

Guano, the more or less modified excrement of sea-birds, occurring on the islands and coasts whence it is obtained, is of very irregular composition, due to the various influences to which it has, in course of time, been exposed, consequently its value, which depends chiefly on the amount of nitrogen and phosphoric acid present, can only be fixed by chemical analysis. The good guano beds of the Chinchas Islands which for a long time supplied all demands and yielded a guano containing on the average 12 per cent. of nitrogen and 12·3 per cent. of phosphoric acid, are now denuded, and the beds worked at present produce an article poorer in nitrogen, but richer in phosphoric acid.*

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* "Anleitung zum Gebrauch des Apparates zur Bestimmung der kohlensauren Kalkerde in der Knochenkohle," by C. SCHEIBLER, printed as MS. 6th edn Berlin, 1874.

In the following pages, an introduction to the analysis of guano is first given, such as generally suffices, and this is followed by the methods to be employed in more complete analyses of guanos.

1. *Determination of Moisture.*

As guano when heated not only gives up water but may also lose ammonia, it is necessary, if this is to be feared, to determine the evolved ammonia along with the moisture.

Frühling and Schulze † recommend the following apparatus for this purpose:

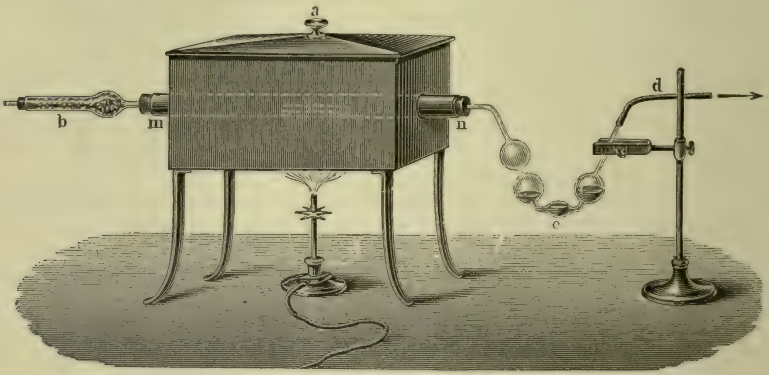

Fig. 133.

About 2 grams of the guano, weighed out in a porcelain boat, is inserted into the glass tube *mn* placed in a water-bath, the bulb-tube *c* containing 10 c.c. of N/2 sulphuric acid, is connected with it, and a slow current of air is drawn through the apparatus by means of a water-pump or aspirator at *d*, the air being dried and freed from ammonia by means of the tube *b*, filled with pumice moistened with concentrated sulphuric acid.‡ After the water in the water-bath has been kept boiling for about an hour, the drying is complete. The loss of weight in the boat containing the guano gives the amount of moisture and evolved ammonia; the amount of the latter may be determined by titrating the contents of *c* with caustic soda or baryta water, the moisture being equivalent to the difference.

2. *Estimation of Nitrogen.*

Nitrogen is for the most part contained in guano as ammonia salts, in lesser degree as uric acid and other organic compounds, and in smallest amount as nitric acid, if any of the latter is present. The total nitrogen and, if present, that in different forms of combination, is determined as in § 328 and § 329. For the estimation of the total nitrogen, 0·5 to 1 gram of substance is sufficient. When KJELDAHL's or VARRENTRAPP and WILL's process is adopted, it is advisable to have 20 c.c. of N/2 sulphuric acid in the receiver. If a combustion with soda-lime is made, the mixing of the substance with the lime is best performed in the combustion tube itself by means of a piece of wire, as when the guano and soda-lime are ground up together in a mortar, an appreciable amount of ammonia is disengaged (see this vol. p. 52).

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* For the occurrence of guano in various parts of the world see E. Heiden's "Lehrbuch der Düngerlehre," 2nd edn. (Phil. Cohen, Hanover, 1884), vol. ii. pt. 2. p. 349.

† His "Anleitung zur Untersuchung der für die Zucker-Industrie in Betracht kommenden Rohmaterialien, &c." (Fr. Vieweg & Son, Brunswick, 1876).

‡ Compare the footnote †, this vol. p. 590.

3. *Estimation of Phosphoric Acid.*

a. Total phosphoric acid.—About 2·5 grams of guano is heated with twice or thrice its weight of a mixture of 2 parts of anhydrous carbonate of soda and 1 part of nitrate of potassa, gently at first, but gradually increasing the heat until the contents of the crucible have become white. When cold, it is softened by warming with water, rinsed into a beaker, and about 30 c.c. of nitric acid of 1·25 sp. gr. is added, by the aid of which also any residue still adhering to the crucible is removed; and the whole, after being heated until all the soluble portion is dissolved, is evaporated to dryness to remove silica, and the residue treated with nitric acid and water, and filtered. The solution is then made up to 250 c.c., and 50 c.c. used for the phosphoric acid determination as in § 309 or § 313, *ββ*.

Instead of the mixture of carbonate of soda and nitrate of potassa, G. GILBERT * employs a mixture of 2 parts of anhydrous carbonate of soda and 1 part of chlorate of potassa. When the mass has become white, it is heated to a bright red heat for another quarter of an hour, and the cold fused mass is then treated as above.

b. Phosphoric acid "soluble in water," and "soluble" as defined in § 316.—If the phosphoric acid soluble in water and that soluble in a solution of citrate of ammonia containing free citric acid (§ 316) are to be estimated separately, 5 grams of the guano is treated with the solvent as in § 312 or § 316 respectively, the undissolved residue washed, and the phosphoric acid in it determined as in *a*, using, however, 100 c.c. of the solution which has been made up to 250 c.c., the "soluble in water" or the "soluble" phosphoric acid being ascertained from the difference.

4. *Total Amount of fixed Constituents.*

Five grams of the guano is incinerated in a porcelain or platinum crucible placed in a slanting position, and the ash weighed. If the analysis of a guano is to be complete, the following estimations must be made:

5. *Fixed Constituents Singly.*

These are determined by the methods described in § 287 and § 289.

6. *Total Amount of Carbon.*

This is determined as in § 327, 5.

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* Zeitschr. f. anal. Chem. 12, 1.

7. *Carbonic Acid.*

This is estimated by one of the methods given in § 139, II., but the most accurate results are obtained by the process described in Vol. I. p. 340. Genuine guano contains only a small proportion of carbonates; so that if a guano effervesces strongly when moistened with dilute hydrochloric acid, this may be regarded as a proof that it is adulterated with carbonate of lime.

8. *Uric acid.*

If it is desired to ascertain the amount of uric acid in a guano containing this compound,* a weighed quantity, not too small, is digested, at a gentle heat, for a few hours, with water to which a little caustic soda has been added; it is then filtered, washed, and the washings are united with the filtrate, after concentrating by evaporation, the whole being acidified with hydrochloric acid, and left for 48 hours at the lowest available temperature. The precipitated uric acid, after being collected on a small filter which has been dried at 100° and weighed, is washed with the smallest possible quantity of ice cold water until the final washings no longer give any reaction for hydrochloric acid, dried at 100°, and weighed.

9. *Oxalic acid.*

The oxalic acid in a guano containing oxalate of ammonia can be determined by boiling 5 grams of the guano with 20 grams of carbonate of soda and about 200 c.c. of water, making up the whole to 500 c.c., when cold, with water, mixing, and finally filtering through a dry filter; 50 or 100 c.c. is acidified with acetic acid, filtered if necessary, and the oxalic acid determined as in § 137 *a*.

10. *Constituents soluble and insoluble in Water.*

10 grams of guano is heated with about 200 c.c. of water, and the residue, collected on a weighed filter without delay, is washed with hot water until the washings no longer have a yellowish tinge and leave no appreciable residue when evaporated on platinum foil; the residue is then dried and weighed. On deducting the sum of the water and the insoluble residue from the total weight of the guano, the difference gives the amount of soluble constituents. By incinerating the insoluble portion, weighing the ash, and deducting it from the value obtained in 4, the sum of the fixed soluble salts is ascertained. In very superior descriptions of guano, the matter insoluble in water amounts to 50–55 per cent., but in the inferior kinds to as much as 80–90 per cent. The brown aqueous solution of good genuine guano evolves ammonia on evaporation, has a urinous odour, and leaves a brown saline mass consisting chiefly of sulphates of soda and potassa, chloride of ammonium, and oxalate, urate, and phosphate of ammonia.†

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* As a qualitative test for uric acid, a little dilute nitric acid is poured on to a small quantity of the guano and the whole evaporated carefully to dryness. If uric acid is present, a yellow or yellowish red residue is left which changes to a beautiful purple red on adding a trace of ammonia (the murexide reaction).

† Although the estimation of the portions soluble and insoluble in water is not without its use in determining the value of a guano, still it must be mentioned that the quality and quantity of the constituents soluble in water are by no

b. Decomposed guano.

The nitrogen in this and also the total phosphoric acid are determined in the same way as in crude guano, the moisture, and the phosphoric acid in its different conditions of solubility, being estimated in the manner prescribed for superphosphate (§ 311 to § 317 incl.).

3. Fish guano, "granat" guano, horn-meal, tendon-meal, and flesh-meal manure.

§ 332.

The manurial substances mentioned in the title owe their value to the nitrogenous organic matter which they contain; and also, but in a lesser degree, to their phosphoric acid. Potash is usually present in such small amount as to be almost or quite out of consideration. The average content* of fish guano is 7 to 9 per cent. of nitrogen and 10 to 13·5 per cent. of phosphoric acid; of "granat" guano 8 per cent. of nitrogen and 3 per cent. of phosphoric acid; of horn-meal 10 per cent. of nitrogen and 5 to 6 per cent. of phosphoric acid; of tendon-meal 9·7 per cent. of nitrogen and 6·3 per cent. of phosphoric acid. In the case of flesh-meal, the proportions of nitrogen and phosphoric acid vary between wide limits.

The *phosphoric acid* and the *nitrogen* are determined in the same manner as in guano, 0·7 to 1 gram of substance being taken for the nitrogen estimation, 20 c.c. of N/2 sulphuric acid being also employed. For *moisture*, *ash* and *sand*, the mode of procedure is the same as for bone-meal.

4. Mixed Manures.

§ 333.

As it is of great importance in agriculture to employ manures, the amount and composition of whose manurial constituents are exactly known, manure manufacturers send out mixed manures of the most varied kinds, guaranteeing the amount, state of combination, and solubility, of the important constituents, that is nitrogen, phosphoric acid, and potash.

These mixed manures may be divided into those having a neutral or alkaline reaction, and those with an acid reaction. To the former

means constant, or characteristic of the same guano. In fact, v. LIEBIG (Ann. d. Chem. u. Pharm. 119, 13) has shown that the kind of salts passing into solution is different according to whether the solution is filtered off immediately or only after some time. In the first case, the solution contains much oxalate and little phosphate, together with some sulphate of ammonia; in the second case, the oxalate of ammonia is more or less completely replaced by phosphate of ammonia, the oxalic acid remaining, combined with lime, in the residue. The cause of this interesting behaviour is that although phosphate of lime, when in contact with oxalate of ammonia and water alone, undergoes scarcely any change, yet it is very soon converted into oxalate of lime, with formation of phosphate of ammonia, if sulphate of ammonia (or chloride of ammonium) is also present, as this renders the phosphate of lime somewhat soluble; the portion dissolved is then at once precipitated by the oxalic acid, and the sulphate of ammonia is thus enabled to act on a fresh portion of phosphate of lime.

* See "Mittlere Zuzammensetzung der Düngemittel," by E. WOLFF (Menzel and V. Lengerke's landwirthschaftlicher Kalendar, 1875).

belong especially those guanos made up to a known composition by the admixture of sulphate of ammonia, chili saltpetre, blood-meal, &c.; to the latter, the mixtures of superphosphates with sulphate of ammonia, chili saltpetre, potash salts, &c. The first-named are analysed by the methods employed for guano (§ 331) or, if containing chili saltpetre, the nitrogen is estimated as in §§ 328 and 329.

Superphosphates containing nitrogen and potash are analysed, as far as moisture and phosphoric acid are concerned (the latter both as a whole and in its different conditions of solubility), by § 311 to § 318 inclusive. With regard to nitrogen, both total and in its different states of combination, according to § 328 and § 329. In making an estimation of the potash, the following process is used:

20 grams of the substance is heated to boiling with about 200 c.c. of water, allowed to settle, poured off into a litre flask, the residue boiled again with about 200 c.c. of water, and the whole rinsed into the litre flask and allowed to cool; it is then made up to the mark with water, shaken, and filtered through a dry filter. For the potash determination, 50 c.c. of the filtrate is taken in the case of manures rich in salts of potassa, or 100 c.c. when poorer in this respect. It is then heated to boiling, after the addition of 100 to 200 c.c. of water, chloride of barium is added carefully, avoiding too great an excess, so long as a precipitate is produced, and the whole is filtered after subsidence. The alkalies, and particularly the potassa, are estimated as in § 287. If the potassa alone has to be determined, the weight of the alkali chlorides is approximately ascertained as a guide to the quantity of platinum chloride solution required. In cases where a high degree of accuracy is desired, the filtered sulphate of baryta must be gently ignited, and then boiled with dilute hydrochloric acid. The filtrate thus obtained must be evaporated to dryness, the residue taken up with water, and this liquid added to the chief solution.

VI. ANALYSIS OF ATMOSPHERIC AIR.

In the analysis of atmospheric air, attention is usually confined to the following constituents: oxygen, nitrogen, carbonic acid, and aqueous vapour. It is only in exceptional cases that the exceedingly minute quantities of ozone, ammonia, and other gases—many of which may be assumed to be always present in infinitesimal traces—are also determined.

It does not come within the scope of the present work to describe all the methods employed in the comprehensive investigations which have been made to establish the relative proportions of oxygen and nitrogen in atmospheric air by BRUNNER, DUMAS and BOUSSINGAULT, BUNSEN, REGNAULT, and REISET, FRANKLAND and WARD, MORLEY, VON JOLLY, KREUSLER, HEMPEL, and others. The author has nothing to add to them, and there is therefore little object in giving abstracts from the original treatises. KREUSLER* has collected all these and especially the methods employed for the estimation of oxygen in the atmosphere, and has also given all the references in his excellent work, so that in this connection his treatise can be consulted. It may, however, be added that, in the interim, a second treatise by HEMPEL has appeared † in which the consensus of all trustworthy investigations, namely, that the proportion of oxygen in atmospheric air varies only between narrow limits, is confirmed.

It is sufficient, therefore, here to describe only such methods as are best adapted for testing atmospheric air for its chief constituents for hygienic or technical purposes, omitting the description of methods for the physical examination of air and for the determination of its content of ozone, ammonia and other gases occurring in minute quantities.‡

A. Determination of the Water and Carbonic Acid.

I. BRUNNER'S Method.

§ 334.

In this method, a measured volume of air is slowly drawn, by means of an aspirator, through an apparatus filled with substances which have the property of retaining the aqueous vapour and the carbonic acid, and then estimating these two constituents by the increase in weight of the apparatus.§

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* "Landwirthschaftliche Jahrbücher," by Dr H. THIEL, 1885, pp. 305 *et seq.*

† Ber. d. deutsch. chem. Gesell. 18, 1800.

‡ C. FLÜGGE gives a comprehensive statement of the relative methods ("Lehrbuch der hygienischen Untersuchungsmethoden," Leipzig, Veit & Co. 1881),—Special introduction to the bacteriological examination of air is given by F. HUEPPE ("Die Methoden der Bakterienforschung," 3rd ed. C. W. Kreidell Wiesbaden, 1886).

§ There are, however, more accurate and far more rapid methods for determining the carbonic acid.

Fig. 134 represents the arrangement recommended by REGNAULT.

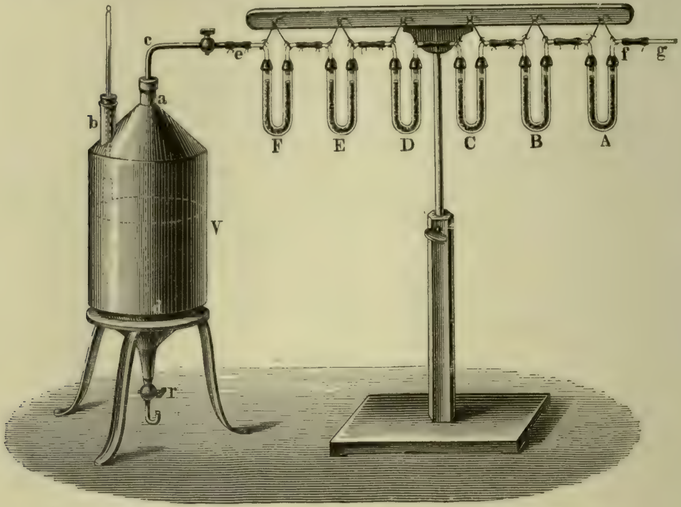

Fig. 134.

The vessel *V*, made of galvanised iron or of sheet zinc, holds from 50 to 100 litres, and stands upon a strong tripod in a pan large enough to hold the whole of the water that *V* contains. At *a*, a brass tube *c*, long enough to reach to the bottom of *V*, and furnished with a stopcock, is firmly fixed with cement; into the aperture *b*, which serves also to fill the apparatus with water, a thermometer reaching down to the middle of *V* is fixed air-tight by means of a perforated cork soaked in wax.

The efflux tube *r*, which is provided with a tap, is bent slightly upward, to guard against any chance of air entering the vessel from below. The capacity of the vessel is ascertained once for all by filling it completely with water, and then accurately measuring the contents in graduated vessels. The end of the tube *c* is connected air-tight with *F*, by means of a caoutchouc tube *e*,* and the tubes *A* to *F* are similarly connected with one another; *A*, *B*, *E*, and *F* are filled with small pieces of pumice† moistened with pure concentrated sulphuric acid, *C* and *D* with moist hydrate of lime.‡ Finally, *A* is also connected with a long tube leading to the place from which the air intended for analysis is to be taken. The corks of the tubes are coated over with sealing wax. The tubes *A* and *B*,* which are intended to withdraw the moisture from the air, are weighed together. *C*, *D*, and *E* are also weighed jointly; *C* and *D* absorb the carbonic acid, and *E* the aqueous vapour which may have been withdrawn from the hydrate of lime by the dry air. *F* need not be weighed; it serves merely to protect *E* against the entrance of aqueous vapour from *V*.

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* As the caoutchouc walls are to a certain extent permeable by moist air (LASPEYRES, DIBBITS), and absorb a little carbonic acid (MUNTZ and AUBIN, SPRING and ROLAND), care must be taken that the ends of the glass tubes connected by the caoutchouc tubing are ground to fit and are pressed tightly together.

† In order to completely cleanse the pieces of pumice from metallic chlorides, they are moistened with concentrated sulphuric acid and heated to redness in a Hessian crucible.

‡ This method of filling the tubes has been again adopted (as far as concerns the lime) in accordance with BRUNNER'S original plan, instead of pouring potash-lye into tubes containing pumice as has also been proposed, because, as HLASIWETZ (Chem. Centralbl. 1856, p. 517) has shown, the potash-lye absorbs oxygen as well as carbonic acid, a fact previously pointed out by H. ROSE. The object may also be attained by the use of soda-lime. For absorbing the water, chloride of calcium

When the aspirator has been completely filled with water, *c* is connected with *F*, and thereby with the entire system of tubes, and the tap *r* is opened a little, just sufficiently to cause a slow efflux of water. When *V* is completely emptied, the height of the thermometer and that of the barometer are noted, and the tubes *A* and *B*, and *C*, *D*, and *E* weighed again.

As the increase in weight of *A* and *B* gives the amount of water, that of *C*, *D*, and *E*, the amount of carbonic acid, and the capacity of *V* (or of the water which has run out of *V*, as the experiment may be varied so that instead of the whole a part only may be allowed to run out, and collected in measuring vessels), the volume of the air (freed from water and carbonic acid) which has passed through the tubes, the calculation is in itself very simple; it involves, however, at least in very accurate analyses, the following corrections:

α. Reduction of the air in *V*, which is saturated with aqueous vapour, to dry air; since the air which penetrates through *c* is dry (see § 198, γ).

β. Reduction of the volume of dry air thus found to 0°, and 760 mm. (§ 198, α and β).

When these calculations have been made, the weight of the air which has passed into *V* is readily found (1000 c.c. of dry air at 0° and 760 mm. weigh 1·2936 grams), and as the carbonic acid and water have also been weighed, the respective quantities of these constituents of the air may now be expressed in per cents by weight, or, calculating the weights into volumes, in per cents by measure.

Considering the great weight and size of the absorption apparatus, as compared with the increase of weight brought about by the process, at least 25000 c.c. of air must be aspirated through it, otherwise considerable errors are likely to arise, more particularly as regards the carbonic acid, the quantity of which in atmospheric air is, on an average,

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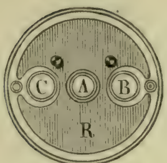
cannot be used, as it does not completely dry the air, and because also, as HLASIWETZ has shown (*loc. cit.* p. 517), traces of chlorine corresponding with the amount of ozone in the air, are carried off. Neither can concentrated sulphuric acid be recommended for very accurate estimations as it retains carbonic acid, although to a very small extent (W. B. and R. E. ROGERS, HLASIWETZ, SPRING and ROLAND). In such cases, the best method is to use anhydrous phosphoric acid, which dries the air a little more thoroughly than sulphuric acid. It must not, however, be employed in U-tubes but in straight tubes inclined upwards, of the form shown in Fig. 12 this vol. p. 10 (DIBBITS, Zeitschr. f. anal. Chem. 15, 156; see also A. MITSCHERLICH, this vol. p. 34, and E. W. MORLEY, Zeitschr. f. anal. Chem. 24, 533).

* In weighing the tubes, care must be taken to allow them to attain, while closed, the temperature of the weighing room. They are then wiped again if necessary, and after being closed by means of ground glass stoppers (which method is to be preferred), or left open, are hung on the balance beam, and weighed after a lapse of 10 minutes. Closing the tubes with caoutchouc is not recommended (DIBBITS, *loc. cit.* p. 160). The balance case must be kept as dry as possible, by the use of large quantities of chloride of calcium.

Fig. 135.



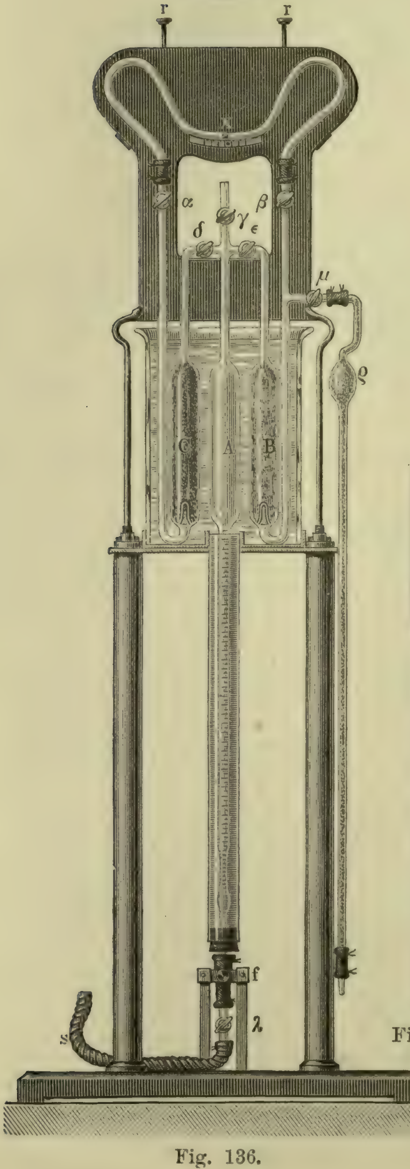


Fig. 136.

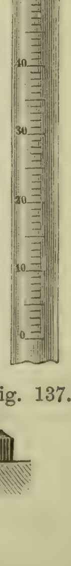


Fig. 137.

only about one-eighth that of the aqueous vapour (comp. Hlasiwetz, *loc. cit.*).

II. Pettersson's method.

§ 335.

Water and carbonic acid can be determined very accurately and much more quickly, in the case of small quantities of air, by the method published by O. Pettersson* which is performed with the aid of the apparatus shown in fig. 136.

A is a 100 c.c. pipette having the lower tube graduated in millimetres (fig. 137). For this a table is calculated showing the amount in parts of a cubic centimetre corresponding with the divisions marked on the tube. The pipette communicates, at the upper end, by a system of narrow but not capillary glass tubes,† on the right hand with a reservoir *B* filled with glass-wool and anhydrous phosphoric acid, and on the left hand with a reservoir *C* containing glass-wool and thoroughly dried soda lime which has been introduced while hot. The system of three reservoirs is immersed in a vessel filled with water, in which a *uniform*, although of course not *constant*, temperature is maintained by means of a stirrer, the handles *rr* of which are visible at the top of fig. 136, the plate *R* being shown in fig. 135.

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* Zeitschr. f. anal. Chem. 25, 467.

† These tubes are shown in fig. 136 half as wide again as they should be, for the sake of clearness, the other parts of the apparatus being as far as possible in correct proportion. The tubes and taps should have a free opening of not less than 1 mm.

The analysis is performed by passing the sample of air measured in the pipette *A*, first into the drying vessel *B*, and, after the air has been brought back into *A*, measuring, by means of the graduated tube, the diminution in volume caused by drying—afterwards the carbonic acid in the dry air is absorbed in the same way in the tube *C*, and the loss in volume is again measured in *A*. In carrying out the analysis, therefore, two distinct kind of operations are involved—(1) the transfer and retransfer of the air from one vessel to another; and (2) the levelling of the mercury in the graduated tube and the measurement of the volume of air enclosed in *A*, after each operation

In carrying out the analysis, *B* and *A* are both first filled with the air under examination, that in *B* being previously dried whilst that in *A* is left unchanged. For this purpose, *A* is completely filled with mercury by the aid of a mercury reservoir—connected with the tap λ by a caoutchouc tube covered with thin flexible copper wire—and suspended by a cord so that it can be raised or lowered at convenience, and again emptied by lowering the mercury reservoir while the taps γ, δ, β are closed and the lower end of the tube ρ containing anhydrous phosphoric acid is in connection, by means of a suitable glass tube, with the space containing the air to be analysed. The dried air then arrives by way of ρ and the tap μ in *B*, which it enters through a short pointed tube covered with a small inverted bell glass. The air previously contained in *B* is hereby driven out and, after repeating the operation several times by suitably opening and closing the taps ϵ and γ, is completely replaced by the air to be tested.

When *B* is filled in this manner, μ is closed, and *A* is filled with the air to be examined. For this purpose, the tap γ is opened, δ and ϵ being closed, *A* is completely filled with mercury, and when the air to be tested is other than that of the room in which the apparatus is placed—the upper outlet of *A* is connected with a glass tube which opens into the space containing the air to be examined, the tube having been previously filled with this air by suction, and the mercury is allowed to run out to about the lower zero on the graduated tube. The glass tap λ is then closed, and the height of the mercury regulated by the screw *f*—which compresses the indiarubber tube uniting the graduated tube with the tap γ, by means of a brass plate—until the mercury is exactly on the zero mark, which can be ascertained by the aid of a lens. The caoutchouc tube, which is compressed by the screw *f*, having sometimes to withstand considerable pressure should be made of thick caoutchouc, and covered, after being fixed in position, by a piece of strong silk, stitched on.

A being thus filled with the air to be tested, δ, ϵ, a, and β are opened in order to equalise the pressure throughout the apparatus, and the stirrer is set in motion so that every part of it may be of the same temperature. The small liquid seal x in the differential manometer, occupying only about 3 to 4 m.m. of the manometer tube δ, and consisting preferably of concentrated sulphuric acid* coloured with indigo-blue, then automatically comes to rest at one of the marks on the small scale.

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* A petroleum of high boiling point makes a still more sensitive index than sulphuric acid.

This must be accurately observed by the aid of a lens, as in each of the succeeding operations the drop must be brought back exactly to the same spot before reading off the volume. The horizontal portion of the manometer tube is slightly depressed in the centre so that the drop naturally assumes a central position. When all the differences of temperature and pressure are adjusted γ, δ, and β are closed, but ϵ is left open; λ is then opened, and the mercury reservoir gradually raised so that *A* slowly fills with mercury and the air is driven from it into *B*. As the dry air already in *B* cannot escape, the pressure naturally increases considerably, and the mercury reservoir must consequently be raised about 130 cm. in order to bring the level of the mercury from the zero mark on the scale tube up to the T shaped branch of the narrow connecting tube above the pipette *A*, so as to completely drive the contents of *A* into *B*.

After about 10 to 20 minutes, the last traces of moisture in the air originally in *A*, and now compressed into *B*, are absorbed. The air is now allowed to return again from *B* into *A* by gradually lowering the mercury reservoir, so that the air in *A* is finally at about the original pressure, the stirrer is set in motion to render the temperature uniform throughout the apparatus, and the tap β is then very cautiously opened, whereupon the little index moves either to the right or left according as the mercury in the graduated tube has been placed too high or too low; λ is now closed, the screw *f* is turned until x has almost resumed its original position, α is then opened carefully, and the index brought to its old position by turning the screw *f*. A few minutes are allowed to elapse to see that it stays there, and, as soon as this is the case, the height of the mercury in the graduated tube is read off. The difference found corresponds with the amount of moisture that was in the air in *A*. If there is any doubt as to whether the absorption of this was complete in *B*, the air may be forced once more from *A* into *B*, and the reading repeated.

When the determination of the moisture is finished, the air in *A* is forced in a similar manner into *C* to allow the carbonic acid to be absorbed; for this purpose, the taps γ, ϵ, and α must be closed, while δ remains open. In 10 minutes, as a rule, the absorption of the carbonic acid is complete, so that on repeating the operation no further decrease in volume is observed in the graduated tube. If, as prescribed, *C* has been filled with highly dried and hot soda-lime, the air after being freed from carbonic acid—at least when the proportion of carbonic acid is that ordinarily found—is so dry that the decrease in volume may be at once read off. Should it be feared that the air in *C* may have again taken up moisture, it must first be redried in *B* and the decrease in volume read off afterwards.

As is evident, variation in the pressure of the external atmosphere cannot affect the measurements, the taps γ and μ being closed during the processes of absorption. The temperature of the whole system, even when kept uniform, is not constant, and therefore the internal pressure varies. As, however, the alteration in volume of the glass vessels *A*, *B*, and *C* as well as that of the air contained in them, is proportional, the effects of the variations of temperature are automatically neutralised, and the determinations, on reference to the calibrating tables, give the percentage by volume of water and of carbonic acid sufficiently accurately for all ordinary analyses. When it becomes a matter of the highest degree of precision, care must be taken that during the experiment the temperature in the system does not vary at all, or only about 0·1°,* as if the variation is equal to a whole degree it will be found that in consequence of the unequal expansion of the anhydrous phosphoric acid in B and the soda-lime in C the compensation will be approximate only and not exact. If, as described, the moisture is first determined and then the carbonic acid, in the same portion of air, it follows that as the mercury level at the completion of the moisture determination will usually be in the wider part of the graduated tube, the decrease in volume corresponding with the carbonic acid will always be read off in this part. If it is desired to read it off in the narrower part, so as to ensure greater accuracy, the tap μ is opened when the determination of the moisture is completed, and so much dry air is admitted through ρ and B to that already in A, that the level of the mercury is again at the lower zero mark on the graduated tube; γ, ϵ, a, and β are then opened for a couple of seconds so that the air in C also is reduced to the atmospheric pressure, γ, a, ϵ, and μ are closed, the dry air contained in A is driven into C, and, after the carbonic acid has been absorbed (which requires 10 minutes), the decrease in volume thus produced is read off in the narrow part of the graduated tube.

The method described is, according to PETTERSSON's experience, accurate to within about 0·002 per cent. If an accuracy to within 0·05 per cent. is sufficient, as is the case in the hygienic examination of the air of rooms for carbonic acid, and the hygrometric determination of atmospheric moisture, PETTERSSON recommends a much smaller apparatus which can readily be carried about in a wooden box, and the pipette A of which holds only 18 c.c.

The water absorption is performed in this by using an Orsat tube filled with concentrated sulphuric acid; the absorption of the carbonic acid, however, is effected by means of dry soda-lime.

The graduated tube in the small apparatus also has a wider and a narrower portion, but the wider part is *below* and serves for the determination of the water, whilst the carbonic acid estimation is performed in the narrow *upper* part of the tube.

The PETTERSSON apparatus naturally requires to be very carefully worked. Those used by PETTERSSON in his investigations were made by FRANZ MÜLLER of Bonn.

B. Estimation of Carbonic Acid Alone.

1. PETTENKOFER's Original Process.†

§ 336.

a. Principle and Requisites.—PETTENKOFER's process consists in causing a known volume of air to act on a definite quantity of baryta water, the strength of which has been ascertained by standardizing it with oxalic acid solution, in such manner that the carbonic acid is completely combined with the baryta. The baryta water is then poured out into a cylinder, allowed to settle with exclusion of air, an aliquot part of the clear liquid is removed, and the baryta remaining in solution is determined. Calculating from a part to the whole, the difference between the oxalic acid required for a certain quantity of baryta water before and after the action of the air, represents the carbonate of baryta formed, and consequently the carbonic acid present.

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* This must be accomplished by keeping the temperature of the room approximately constant, and not by raising or lowering the temperature of the water reservoir by the addition of hot or cold water.

† Abhandl. der naturwiss. u. techn. Commission der k. bayer. Akad. der Wiss. II. 1; Ann. d. Chem. u. Pharm., II. Supplementband p. 1.

For the absorption of larger quantities of carbonic acid, baryta water is used which contains 21 grams of crystallized hydrate of baryta* in the litre, a weaker solution containing 7 grams of hydrate of baryta serving for the absorption of smaller quantities of carbonic acid. 1 c.c. of the stronger corresponds with 3 milligrams of carbonic acid, and 1 c.c. of the weaker with 1 milligram. The solutions of baryta are kept in bottles similar to those figured on page 314 of this volume; the tubes *b* and *c* contain pumice steeped in solution of potash; the bottle *d* may be omitted.

The oxalic acid solution which serves for standardizing the baryta water contains 2·8636 grams of crystallized oxalic acid in 1 litre; this must be neither effloresced nor moist.† 1 c.c. of this solution corresponds with 1 milligram of carbonic acid. If, therefore, the number of c.c. of oxalic acid solution required to neutralise the baryta water is known, the number of milligrams of carbonic acid is also known. The baryta water is standardized by transferring 30 c.c. of it to a flask, and then gradually running in the oxalic acid from a burette with an ERDMANN'S float, the liquid being shaken from time to time, closing the mouth of the flask with the thumb. The end point of the alkaline reaction is ascertained with delicate turmeric paper.‡ The addition of the oxalic acid solution is stopped as soon as a drop of the liquid placed on the turmeric paper with a glass rod ceases to give a brown ring. If it is necessary, in the first experiment, to take out too many drops for testing with the turmeric paper, the result must be considered as approximate only, and in a second experiment, the whole quantity of oxalic acid to within 1 or ½ c.c. is added at once, and the testing with turmeric paper is then begun. A third experiment would be found to agree with the second within 1/10 c.c. The reaction is so sensitive that all foreign alkaline matter, particles of ash, tobacco smoke, &c., must be carefully guarded against.

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* The hydrate of baryta used for preparing the baryta water must be entirely free from caustic potash or soda, the smallest quantities of which render the volumetric estimation impossible if carbonate of baryta is present, as the neutral alkali oxalates decompose the alkaline earth carbonates. When even a minute quantity, therefore, of carbonate of baryta is suspended in the liquid—and this is always the case when a baryta water which has been used for the absorption of carbonic acid is not filtered—the reaction continues alkaline if the smallest trace of potash or soda is present, because the alkali oxalate formed immediately enters into reaction with the carbonate of baryta. A fresh addition of oxalic acid converts the alkali carbonate again into oxalate, and the liquid is for a moment neutral, until, on shaking with air, the carbonic acid escapes, and any carbonate of baryta still present converts the alkali oxalate again into carbonate. To test a baryta water for caustic alkali, the alkalinity of a perfectly clear portion is determined, and then of another portion that has been mixed with a little pure precipitated carbonate of baryta. If in the second experiment more oxalic acid is used than in the first, caustic alkali is present, and some chloride of barium must be added to the baryta water before it can be used.

† This is obtained pure by decomposing oxalate of lead with dilute sulphuric acid; other methods of preparation are given in this vol. p. 192. As regards drying it, see Vol. I. p. 102.

‡ This is prepared with Swedish filter paper free from lime, and tincture of turmeric made with spirit which is free from acid; the paper is dried in a dark room, and must be kept protected from the light. It should be of a lemon yellow colour.

b. The actual Analysis.—On the principles just laid down, the estimation of carbonic acid may be effected in different ways.

α. A perfectly *dry* bottle, of about 6 litres capacity, with well-fitting ground glass stopper, the capacity of which has been accurately determined, is filled, by means of a pair of bellows, with the air to be analysed; 45 c.c. of the dilute standard baryta water is added, and spread over the inner surface of the bottle by turning the latter about, but without much shaking. In the course of about half an hour, the whole of the carbonic acid is absorbed. The turbid baryta water is poured into a cylinder, closed securely, and allowed to settle; 30 c.c. of the clear supernatant liquid is then taken out, by means of a pipette, and titrated by the standard oxalic acid solution; the volume used is multiplied by 1·5 (as only 30 c.c. of the original 45 are employed in this experiment), and the product deducted from the number of c.c. of oxalic acid used for titrating the 45 c.c. of fresh baryta water; the difference represents the quantity of baryta converted into carbonate, and consequently the amount of the carbonic acid. If the air is unusually rich in carbonic acid, the concentrated baryta water must be employed.

β. The air is passed through a tube or through two tubes containing measured quantities of standard baryta water, and the experiment finished as in *α*. For passing a definite quantity of air, an aspirator is generally employed (this vol. p. 590); PETTENKOFER in his experiments with the respiration apparatus forced the air by means of small mercurial pumps first through the tubes, and then through an apparatus for measuring the gas. The form and arrangement of the tubes is illustrated by fig. 138. Two such tubes were used; the first was filled for the length of 1 metre, the second for 0·3 metre, with baryta water, the former with the stronger solution, the latter with the weaker. The tubes lie in a brass holder lined with caoutchouc and cork, and can by means of pointers, levels, and binding screws be fixed at any desired inclination, the latter being chosen so that the single bubbles of air which enter through the short arms of the tubes and are carried

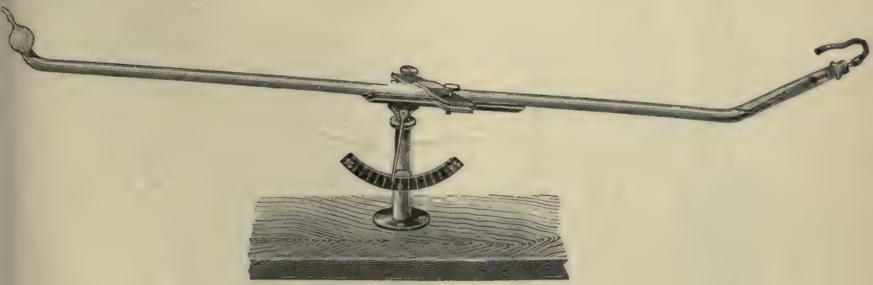

Fig. 138.

beyond the bends by a narrow flexible tube, move on with the necessary rapidity without uniting. The motion of the gas bubbles keeps up a constant mixing of the baryta water. If the air is sucked through by means of an aspirator, a water manometer is necessary to ascertain the true volume of the air. The pressure reduced to mercurial pressure must be subtracted from the reading of the barometer.

II. Modifications of PETTENKOFER'S Process.

1. *Such as refer to the method described in a.*

§ 337.

As in filling a flask which contains about 6 litres by means of a bellows, the object can only be attained with certainty after long continued blowing, and the unavoidable noise is sometimes (in churches, schools, theatres) very disturbing, KL. SONDÉN* recommends the following apparatus for filling the flask with the air to be tested. It can, however, only be used in comparatively large spaces, as in small ones the carbonic acid from the combustion of the paraffin exerts an appreciable influence.

a in fig. 139 is a paraffin lamp enclosed in a tin cylinder *b*, the lamp-glass extending into the chimney *c*, 75 cm. long. The tin cylinder *b* rests on a foot-plate *e* by which it is closed below. The tin side tube *d* carries on its upper extremity a caoutchouc ring whose opening corresponds with that in the bottom of the flask *g* and prevents the admission of air sideways. When the lamp is lighted, a current of air is set up in the direction indicated by the arrows, with the result that a 6 litre flask can be filled with a fresh supply of air in less than a minute and a half. By leaving the lamp to act for 5 minutes, the object is effected with still greater certainty. The neck of the flask *g* and the opening in the base of it are then closed with caoutchouc stoppers.

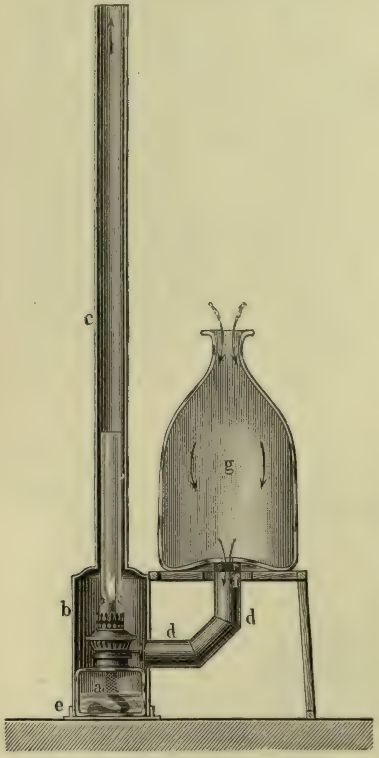

Fig. 139.

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* "Arbeten frän Stockholms Helsovärdsnämds Laboratorium." Stockholm, pub. by K. L. Beckmann, 1886, p. 14.

2. *Modifications of the method described in β.*

§ 338.

W. Spring and L. Roland who are intimately associated with the determination of carbonic acid in atmospheric air,* modified Pettenkofer's absorption tubes in the manner shown in fig. 140.

As may be seen, the tubes can be closed by glass taps at *R* and *r*. They are 1·1 metres long, 14 mm. internal diameter, and are fixed at a slight inclination, so that an air-bubble entering at *B* or *b′*, takes 12 to 15 seconds to pass through one of the tubes, which are filled with baryta water. *E* and *E′* are graduations showing the capacity of the tubes in c.c.; these graduations serve to indicate the degree of evaporation which the baryta water undergoes by the passage of the air. It may be observed in this place that the lower tube only serves, at first, as a check to ascertain whether all the carbonic acid has been absorbed in the upper tube. According to the experience of Spring and Roland it is found that when the experiment is performed according to the directions, and only about 1000 litres of air are passed through the tubes, no turbidity occurs in the second, but after the passage of 30,000 litres of air then a decided precipitate of carbonate of baryta makes its appearance in the second tube. The tube *T* leads to the space containing the air to be tested,† and *S* to an aspirator of about 115 litres capacity and resembling in all essential particulars that described in this vol, p. 590. The effluent

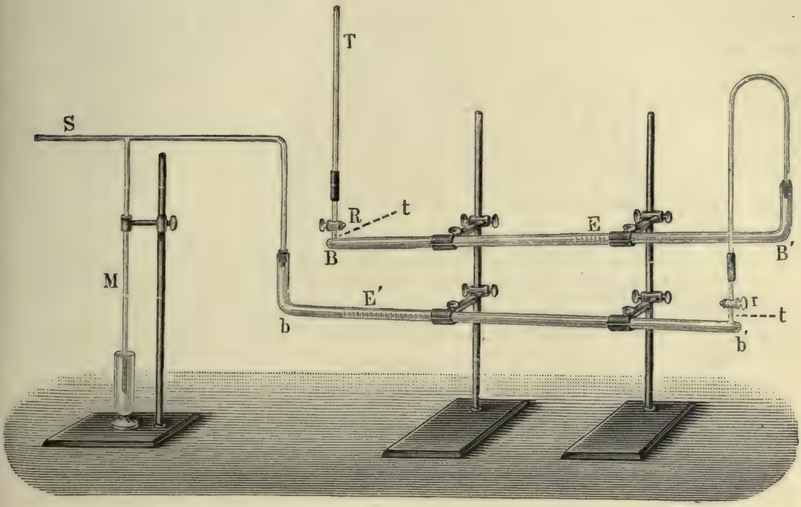

Fig. 140.

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* "Recherches sur les proportions d'acide carbonique contenues dans l'air." Brussels, pub. by F. Hayez, 1885.

† If it is desired to bring it into the tubes in a dry condition, concentrated sulphuric acid cannot be recommended as the drying agent (Spring and Roland, *loc. cit.* p. 64); a tube filled with anhydrous phosphoric acid is best for the purpose; see this vol. p. 591, footnote.

tube of the aspirator is of glass, and dips into a water tank provided with an overflow spout. From the height of water in the tube, the state of rarefaction of the air in the apparatus at the completion of an operation can be ascertained. The water monometer *M* serves as a control, whilst a thermometer reaching into the aspirator indicates the temperature of the air in it.

The tubes are filled with baryta saturated at a relatively low temperature, so that during the experiment its temperature is rather increased than diminished, and any separation of crystals of hydrate of baryta from the solution is with certainty avoided. The baryta water is prepared by dissolving crystals of baryta in water by the aid of heat and leaving the unfiltered solution to cool. As the baryta crystals always contain some carbonate of baryta, one is certain also of obtaining in this way a baryta water saturated with carbonate of baryta.

The tubes are first of all rinsed out with hydrochloric acid, then with water, and finally several times with the baryta water to be employed. They are then left, with closed taps, to drain thoroughly, and with that object they should be suspended vertically, the taps being at the top. After this, 125 c.c. of the titrated baryta water is introduced into each tube by means of a pipette, the tubes are suspended vertically with the taps downwards, and the height of the liquid is read off on the graduated scales *E* and *E′*, the tubes are then brought into the positions shown in fig. 140, the whole apparatus is arranged, the taps *R* and *r* opened, and then the effluent tap of the aspirator to such an extent that each bubble of air takes from 12 to 15 seconds to pass through one tube; in this case, 10 to 12 hours are required to empty the aspirator. The height of the water in the outflow pipe of the aspirator is now measured, and also that in the manometer *M*, and the number of millimetres is divided by 13·5 to calculate water pressure to mercury pressure; the height of the barometer and of the thermometer in the aspirator are next read off, and by the aid of these figures the volume of air drawn through the tubes, reduced to 0° and 760 mm. pressure and in a dry state, is calculated (see § 198). From this volume, the weight of the air can be ascertained by multiplying the number of litres by 1·2936.

Before proceeding to the determination of the caustic baryta remaining in the tube *B B′*, or in both tubes, they are once more fixed in a vertical position with the taps downwards, and these carefully opened, if necessary, to remove any slight quantity of air left in *t*; the height of the liquid is read off on the graduated scales *E* and *E′*. In this way, the loss in volume the 125 c.c. of baryta has sustained by evaporation is ascertained, and must be taken into account in making the calculations.

The contents of the tubes may be either treated in the manner Pettenkofer directs, that is, the baryta water rendered turbid by carbonate of baryta may be left to subside in closed flasks, or the carbonate of baryta may be filtered off. If the latter method be adopted, the fact observed by A. Müller (see Vol. I. 336), that filter paper retains hydrate of baryta, must be taken into consideration. The filters employed must, therefore, always be identical, and the quantity of baryta retained by them when 125 c.c. of baryta water of the same strength as that used in the experiment is filtered, must be ascertained, and the proper correction made. Spring and Roland give the latter method the preference.

3. *Modifications in the manner of titrating the baryta water.*

§ 339.

Whilst PETTENKOFER recommends titrating the baryta water with oxalic acid, using turmeric paper as indicator, SPRING and ROLAND (*loc. cit.* p. 51) give the preference to hydrochloric acid and tincture of litmus, using an acid, 1 c.c. of which corresponds with 0·010 gram of carbonic acid; they also point out (*loc. cit.* p. 71, *et seq.*) that glass vessels when not previously rinsed out with baryta water, convert appreciable quantities of the baryta into an insoluble compound, and on this account they first rinse out with baryta water both the absorption tubes and the measuring pipette, and drain them before using them. REISET gives sulphuric acid the preference; KL. SONDÉN also employs it, diluted so that 1 c.c. corresponds with 1 milligram of carbonic acid, and in order to exclude as far as possible the influence of atmospheric carbonic acid on the baryta water, he recommends* that the 50 c.c. to be titrated should be taken up by a pipette provided with a protecting soda lime tube. The contents are emptied out into a flask, and phenolphtalein added, followed by sulphuric acid until colourless (see this vol. p. 200). Precisely the same quantity of acid as that just employed is now measured into another flask and phenolphtalein is added, followed by another 50 c.c. of baryta water, in such a way that the point of the pipette is below the surface of the acid. To the red liquid, sulphuric acid is now carefully added until the colour just disappears, the acid used being considered as the correct amount. It will be seen that in operating in this way the atmospheric air only remains in contact for a few moments with the liquid, still slightly alkaline from baryta. SONDÉN, by the employment of this method, obtained the figures published by him in the Zeitschr. f. analyt. Chem., Vol. 25, p. 478, and compared them with those obtained by PETTERSSON's method.

III. Process proposed by FR. MOHR, and employed and tested by HLASIWETZ and H. v. GILM.†

§ 340.

This, like PETTENKOFER's method, consists in drawing a large quantity of air, 60 litres at least, through a long, slightly inclined, tube containing pieces of glass and clear baryta water, collecting the carbonate of baryta with exclusion of air, and washing the tubes and the precipitate on the filter, first with distilled water saturated with carbonate of baryta, and then with pure boiled water. Finally the carbonate of baryta still contained in the tubes and that on the filter is dissolved in dilute hydrochloric acid, the solution evaporated to dryness, the residue gently ignited, and the chlorine in the chloride of barium found estimated as in § 141, *b a.*, reckoning 1 equiv. of carbonic acid for each equiv. of chlorine. The amount of baryta in the hydrochloric acid solution may also be determined by precipitation with sulphuric acid. For filtering off the carbonate of baryta, v. GILM employed a double funnel, fig. 141; the inner cork has, besides the perforation through which the neck of the funnel passes, a lateral slit, which establishes a communication between the air in the outer funnel and the air in the bottle.

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* Communicated by letter.

† Chem. Centralbl. 1857, p. 760.

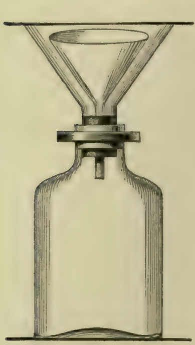

Fig. 141.

Fr. Mohr* subsequently recommended as the absorbent a solution of baryta in potash; to prepare it, crystals of hydrate of baryta are dissolved in a weak solution of potash with the aid of heat, and the carbonate of baryta which invariably forms in small quantity is filtered off. The clear filtrate is thereby saturated with carbonate of baryta; Mohr now leaves out the fragments of glass.

By this method, v. Gilm obtained very concordant results; nevertheless, it involves sources of error, independent of the unavoidable effect of the atmospheric air during filtering. If clear baryta water is passed through paper with the most careful possible exclusion of air, and the filter is washed until the washings are free from baryta, and dilute hydrochloric acid is then poured on to the filter, the filtrate thus obtained, when evaporated, will leave a small quantity of chloride of barium corresponding with the small amount of baryta which has been retained by the paper. A correction must also be made for the baryta rendered insoluble by the surface of the glass vessel (see § 339).

C. Determination of Oxygen and Nitrogen.

§ 341.

As already mentioned, the methods for the *accurate* determination of the proportions of oxygen and nitrogen in atmospheric air, already referred to in this vol. p. 589, will not be treated of here. Those desirous of investigating this subject must not only make themselves well acquainted with the several original treatises, but also be experienced in gas analysis, for which the works of R. Bunsen,† W. Hempel,‡ and Cl. Winkler§ especially will be found to be of very great assistance.

The method proposed by von Liebig|| for the approximate estimation of oxygen will be described here; it is useful when it is required to estimate the amount of oxygen in the air in a more or less confined space, within 0·1 or 0·2 per cent. of the volume, in a short time and without the use of complicated apparatus.

Liebig's method is founded upon the observation made by Chevreul and Döbereiner, that pyrogallic acid, in alkaline solutions, has a powerful tendency to absorb oxygen.

1. A strong measuring tube, holding 30 c.c. and divided into 1/5 or

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* Lehrbuch der Titrirmethode, 5te Aufl. p. 526.

† "Gasometrische Methoden," by Rob. Bunsen, 2nd edn., F. Vieweg & Son, Brunswick, 1877.

‡ Walther Hempel, "Neue Methoden zur Analyse der Gase," F. Vieweg & Son, Brunswick, 1880.

§ Clemens Winkler, "Lehrbuch der technischen Gasanalyse," J. G. Engelhardt, Freiberg, 1885.

|| Ann. d. Chem. u. Pharm. 77, 107.

1/10 c.c., is two-thirds filled with the air intended for analysis. The remaining portion of the tube is filled with mercury, and inverted in that liquid contained in a tall cylinder, widened at the top, fig. 142.

2. The volume of the confined air is measured (§ 12). If it is intended also to estimate the carbonic acid in it, which can be done with sufficient accuracy only if the quantity of the latter amounts to several per cent., the air is dried by introducing a ball of chloride of calcium (§ 16), before measuring. If the carbonic acid is not to be determined, this operation is omitted. A quantity of solution of potassa of 1·4 sp. gr. (1 part of dry hydrate of potassa to 2 parts of water *), amounting to from 1/40 to 1/50 of the volume of the air, is then introduced into the measuring tube by means of a pipette having the point bent upwards, fig. 143, and spread over the entire inner surface of the tube by moving the latter rapidly up and down (see this vol. p. 39); when there is no further diminution of volume, the decrease is read off. If the air has been dried previously with chloride of calcium, the diminution of the volume expresses exactly the amount of carbonic acid contained in the air; otherwise it does not, as the strong potash solution absorbs aqueous vapour.

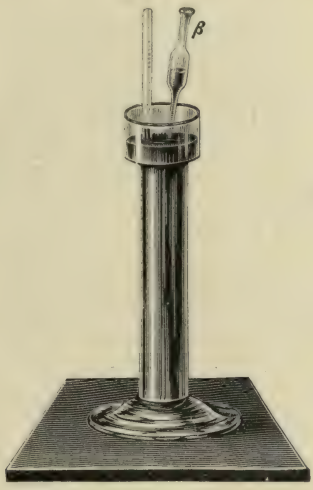

Fig. 142.

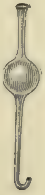

Fig. 143.

3. When the carbonic acid has been removed, a solution of pyrogallic acid, containing 1 gram of the acid in 5 or 6 c.c. of water,* is introduced into the same measuring tube by means of another similar pipette, the quantity of pyrogallic acid solution being half the volume of the potash solution. The mixed liquids (the pyrogallic acid and solution of potassa) are spread over the inner surface of the tube by shaking the latter, as in the process of estimating the carbonic acid, and, when no further diminution of volume is observed, the residuary nitrogen is measured.

4. When the solution of pyrogallic acid mixes with the solution of potassa, it dilutes it, thus causing an error from the diminution of its tension, but this is so trifling that it has no appreciable influence on the results; it may, besides, be readily corrected by introducing into the tube, after the absorption of the oxygen, a small piece of hydrate of potassa corresponding with the amount of water in the solution of the pyrogallic acid.

5. There is, however, another source of error in this method; as a

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* These are the quantities and the concentration of the potassa and pyrogallic acid solutions recommended by Liebig, but they can of course be varied somewhat—see 6.

portion of the liquid always adheres to the inner surface of the tube, the volume of the gas cannot be read off with absolute accuracy. In comparative analyses, the influence of this defect on the results may be almost entirely neutralized, by taking nearly equal volumes of air in the several analyses.*

6. The volume of nitrogen will finally, under certain circumstances, be found to be a little too high owing to the fact—pointed out by Calvert, Cloëz, and Boussingault—that by the action of solution of potassa on pyrogallic acid some carbon monoxide may be formed, and remain unabsorbed along with the nitrogen. The author speaks advisedly in saying *may* be formed, for according to W. Hempel † this does not occur, for example, when one volume of a 25 per cent. solution of pyrogallic acid is mixed with six times its volume of caustic alkali solution of about 60 per cent.

7. Notwithstanding these small sources of error, the results obtained by this method are very accurate and constant. In eleven analyses which v. Liebig published, the greatest difference in the amount of oxygen found was between 20·75 and 21·03. The numbers given express the actual results without any correction.

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* As stated, this vol. p. 165, Bunsen (Gasometrischen Methoden, 2 Aufl. p. 94) employs for the absorption of oxygen a papier-maché ball saturated with a concentrated alkaline solution of pyrogallate of potassa ; this he introduces into the gaseous mixture attached to a platinum wire, repeating the operation several times. By adopting this method of procedure, the source of error mentioned in 5 is avoided.

† Ber. deutsch. chem. Ges. 18, 278.

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PART III.

EXERCISES FOR PRACTICE.

EXERCISES FOR PRACTICE.

In the following pages there are sixty exercises, especially designed for teaching the theory and practice of quantitative chemical analysis. They are almost identical with those which have been set in the author's own laboratory during many years, so that it can be confidently stated that they can all be easily carried out, and that the order of arrangement has been found satisfactory. A glance at this section will show that a few volumetric methods are inserted among the gravimetric problems. By this variation the monotony of the gravimetric operations has been varied in a useful manner, whilst the hurried manner of working into which beginners are easily apt to be betrayed by a continuous course of volumetric analysis is obviated; moreover, the knowledge that in the realm of analysis very different ways lead to the same end is properly imparted, and the mind stimulated to make comparisons of the various methods and to judge them critically.

The principal point kept in view in the selection of these exercises, is that most of them, and more particularly the earlier ones, should permit of an exact control of the results. This is of the utmost importance for analytical students, since a certain amount of self-reliance is amongst the most indispensable requisites for a successful pursuit of quantitative investigations, and this is only to be attained by ascertaining for one's self how near the results found approach the truth.

Now a rigorously accurate control is practicable only in the analysis of pure salts of known composition, or of mixtures composed of definite proportions of pure compounds. When the student has acquired, in the analysis of such substances, the necessary self-reliance, he may proceed to the analysis of minerals or industrial products in which such rigorous control is unattainable.

The second point kept in view in the selection of these exercises, was to make them comprise both the more important analytical methods and the most important substances, so as to afford the student the opportunity of acquiring a knowledge as thorough as possible of every branch of quantitative analysis; naturally, therefore, the most simple methods have not always been employed.

The exercises in elementary organic analysis are, on this account, less numerous and offer far less variety than the analysis of inorganic substances. It is better, therefore, to analyse one and the same organic substance repeatedly until the results are quite satisfactory, than to take fresh substances.

Finally, it may be observed it is not strictly intended that every student should go through the whole of the examples, for it naturally depends a good deal on individual attainments as to how long may be required to make any one a good analyst, it being possible to become such without having made determinations of *all* the substances, or employed *all* the methods. The student must be warned, however, against yielding too soon to the impulse for discovering something new—that is, before he is well up in chemistry especially, and also in practical analysis. Such ambitious methods of hurrying forward in study always, as the author has had frequent occasion of observing, lead to bad results. A building erected on an unstable foundation cannot be permanent.

EXERCISES.

A. Simple Determinations in the Gravimetric way, intended to teach the Student the more common Analytical Operations.

1. Iron.

About 0·3 gram of fine pianoforte wire is weighed on a watch-glass, and dissolved in dilute hydrochloric acid of sp. gr. 1·12, to which about an equal volume of water has been added.

Dissolution is effected by heating in a moderate sized beaker covered with a watch-glass. When the iron is completely dissolved, a little nitric acid is added, the whole heated until it begins to boil, and then a little more nitric acid, to be certain that all the iron is present as ferric chloride (otherwise some more nitric acid must be added). The solution is now transferred to a large porcelain basin, the beaker and the watch-glass rinsed out, the solution which now measures 200 to 300 c.c. is heated to incipient ebullition, ammonia added in moderate excess, filtered through a filter exhausted with hydrochloric acid, &c. (Comp. § 113, 1, *a.*)

As the ferric oxide generally contains a small quantity of silicic acid (arising partly from the silicon in the wire, and partly taken up from the glass vessels), after it is weighed, it must be dissolved by digesting it with fuming hydrochloric acid, with the addition of a few drops of stannous chloride, diluted, the silica collected on a small filter, ignited and weighed; the weight is the silica plus the ashes of both filters. The residue should be white; if it is red, this indicates that some of the ferric oxide has remained undissolved.

The best way of writing down an analysis is here given once for all, the present example being all the better for this purpose as it is somewhat complicated.

Watch-glass + iron	10·3192 gram
„ „ empty	9·9750 „
Iron	0·3442 „
Crucible + ferric oxide + silica + filter ash	17·0703 gram
„ empty	16·5761 „
	0·4942 „
Ash of large filter	0·0008 „
Ferric oxide + silica	0·4934 „

Crucible + silica + ashes of both filters	16·5809	gram
„ empty	16·5761	„
	0·0048	„
Ashes of the filters	0·0014	„
Silica	0·0034	„

0·4934 – 0·0034 = 0·4900 ferric oxide = 0·343 iron which gives 99·65 per cent.

2. ACETATE OF LEAD.

Estimation of Oxide of Lead.—The dried and non-effloresced crystals are triturated in a porcelain mortar, and the powder pressed between sheets of blotting paper until fresh sheets are no longer moistened by it.

a. About 1 gram is weighed out, dissolved in 100 c.c. of water, with the addition of a few drops of acetic acid, and treated exactly as in § 116, 1, *a.*

b. About 1 gram is weighed out, dissolved in 50 c.c. of water, with the addition of a few drops of acetic acid, and treated exactly as directed in § 116, 3, *a*, *a*.

PbO	111·50	58·84
$C_4H_3O_3$	51·00	26·91
3aq.	27·00	14·25
	189·50	100·00

3. ARSENIOUS ACID.

About 0·2 gram of pure arsenious acid in small lumps is dissolved, in a flask of about 500 c.c. capacity, in some solution of soda, by digesting it on the water-bath; it is then diluted with water, hydrochloric acid added in excess, the flask nearly filled with distilled water, and sulphuretted hydrogen passed in, without access of air and without warming, until it is in excess, proceeding, in all other respects, exactly as directed in § 127, 4, *a*. A pair of watch-glasses should be used in drying the filter.

As	75	75·76
3O	24	24·24
	99	100·00

4. POTASH ALUM.

Estimation of Alumina.—Pure, powdered potash alum is pressed between sheets of blotting paper; about 2 grams is weighed out, dissolved in about 300 c.c. of water, and the alumina determined as in § 105, *a*.

KO	47·13	9·93
Al_2O_3	51·50	10·85
$4SO_3$	160·00	33·71
24Aq	216·00	45·51
	474·63	100·00

5. DICHROMATE OF POTASSA.

Estimation of Chromium.

a. Pure dichromate of potassa is melted at a gentle heat, 0·4–0·6 gram is weighed out, dissolved in water in a porcelain basin, and reduced with hydrochloric acid and alcohol; after the latter has been driven off by heating on the water-bath, the residue is diluted with about 200 c.c. of water, and the determination of the chromium is made exactly as in § 130, I. *a*, *α*.

b. About 0·2 gram is again weighed out, dissolved in water, and the solution, measuring about 100 c.c., is precipitated with mercurous nitrate (§ 130. I. *a* *β*). The precipitation is best effected at the boiling temperature, and the washing with hot water to which a little mercurous nitrate has been added.

KO	47·13	31·93
$2CrO_3$	100·48	68·07
	147·61	100·00

6. CHLORIDE OF SODIUM.

Estimation of Chlorine.—Pure chloride of sodium is dried by heating in a platinum crucible (Vol. I. p. 355), about 0·4 gram of it is dissolved in about 100 c.c. of water, and the chlorine determined as in § 141, I., *a*.

Na	23·04	39·38
Cl	35·46	60·62
	58·50	100·00

B. Complete Analysis of Salts in the Gravimetric way. Calculation of the Formulæ from the results obtained. (§§ 202, 203.)

7. CARBONATE OF LIME.

Pure carbonate of lime in powder (whether Iceland spar or the artificially prepared substance) is heated gently in a platinum crucible.

a. Estimation of Lime.—About 1 gram of carbonate of lime is dissolved in dilute hydrochloric acid in a covered beaker, adding water and heating gently until the carbonic acid is completely expelled; it is then diluted to about 300 c.c., and the lime determined as directed in § 103, 2, *b*, *α*.

For control, the carbonate of lime is converted into the sulphate and weighed as such. For that purpose it is transferred to a tared platinum dish, and dissolved in highly diluted hydrochloric acid, covering the dish with a watch-glass which is afterwards rinsed, then proceeding according to § 103, 1. *b*.

b. Estimation of Carbonic Acid.—The carbonic acid is determined in about 0·8 gram, as in § 139, II., *c*.

CaO	28	56·00
CO_2	22	44·00
	50	100·00

8. Sulphate of Copper.

A complete analysis of this should be made. The pure crystals are ground up in a porcelain mortar, and pressed between blotting paper.

a. Determination of the Water of Crystallization.—An empty bulb tube is weighed, half filled with sulphate of copper,* and after being weighed again, is placed in an air-bath with openings in its sides (Vol. I. p. 48, fig. 38), and treated as directed in § 29, using a current of dried air. When no more water escapes at 120°–140°, and repeated weighings of the bulb tube give constant results, the diminution in weight will give the amount of water of crystallization in the salt. An ordinary wide glass tube may be used instead of a bulb tube, the sulphate of copper being placed in a boat, and the latter inserted into the tube and heated as above described. To guard against the reabsorption of water by the dehydrated sulphate of copper during the process of weighing, the boat should always be weighed in a tube, closed by a light glass stopper or by a cork which is weighed along with it both before and after the heating, a wire being twisted round the tube near the stopper and bent so that the ends of the wire serve as feet. In this way, the tube will be prevented from turning round on its axis, and the contents of the boat from falling out. Care must be taken that the thermometer reaches to the proper depth in the air-bath, otherwise it may not indicate the actual temperature of the copper salt.

b. Determination of Water of Halhydration.—The experiment is continued, raising the temperature to between 250° and 260°. The additional loss of weight of the bulb tube gives the amount of the more strongly combined water of halhydration. In order to raise the temperature sufficiently high, it will be necessary to use two lamps if the pressure of the gas is low.

c. Estimation of Sulphuric Acid.—Another portion of the sulphate of copper (about 1·5 grams) is dissolved in about 200 c.c. of water, and the sulphuric acid determined as in § 132, I., 1.

d. Estimation of Oxide of Copper.—About 1·5 grams is dissolved in about 200 c.c. of water, and the oxide of copper determined as directed in § 119, 1, *a*, using pure potash solution.

CuO	39·70	31·83
SO	40·00	32·08
HO	9·00	7·22
4aq	36·00	28·87
	124·70	100·00

9. Crystallized Phosphate of Soda.

a. Determination of the Water of Crystallization.—A platinum crucible containing about 4 grams of clean quartz sand, is ignited and weighed; about 1 gram of finely powdered phosphate of soda which has been dried between blotting paper is introduced, and the whole heated at 100° until the weight is constant; the loss of weight gives the amount of water of crystallization.

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* This is effected by pushing into one end of the tube, down to the bulb, a glass rod with paper folded round it, and filling in the salt through the other end. The tube is then restored to a horizontal position, and gently tapped on the table; the glass rod is withdrawn, and the ends are, if necessary, cleaned with a feather.

b. Determination of the Water of Constitution.—The residue obtained in *a* is ignited.

c. Estimation of Phosphoric Acid.

- *α.* 1·0–1·5 grams of phosphate of soda dissolved in about 200 c.c. of water is treated as directed § 134, *b*, *α*.
- *β.* About 0·5 gram of phosphate of soda dissolved in 40 to 50 c.c. of water, is treated as in § 134, *b*, *β*. Comp. also § 309, *a*, *aa*.

d. Estimation of Soda.—About 1·5 grams of phosphate of soda is dissolved in about 150 c.c. of water, and treated as in § 135, *d*, *β*. After the excess of silver has been separated by hydrochloric acid, the solution is repeatedly evaporated to dryness in a porcelain dish with hydrochloric acid, to expel all the nitric acid. This having been effected, the residue is dissolved in a little water, the solution transferred to a platinum dish, and the chloride of sodium weighed in this; comp. § 98, 3.

If the weighing has taken rather a long time, the chloride of sodium easily absorbs a little moisture, and the weight will be slightly too high. It is advisable, therefore, to re-heat after weighing, allow it to cool in a desiccator, place the weights from the first weighing in one pan of the balance and the dish containing the chloride of sodium in the other, and complete the weighing quickly, when accurate results will be obtained.

PO_5	71·00	19·83
2NaO	62·08	17·34
HO	9·00	2·51
24aq	216·00	60·32
	358·08	100·00

10. CHLORIDE OF SILVER.

About 2 grams of pure fused chloride of silver is ignited in a stream of pure dry hydrogen * until completely decomposed, and the silver obtained is weighed. The ignition may be performed in a light bulb tube, or in a bent glass tube, or in a porcelain boat in a glass tube, or in a porcelain crucible with perforated cover (§ 115, 4, *a*).

The amount of chlorine is found by difference.

Ag	107·93	75·27
Cl	35·46	24·73
	143·39	100·00

11. CINNABAR, SULPHIDE OF MERCURY.

This must be reduced to a fine powder and dried at 100°, most conveniently in a pair of watch-glasses.

a. Estimation of Sulphur.—About 0·5 gram is treated according to § 148 II. A 2, *a*, *β* (Vol. I. p. 387). The operation should be performed in the open air or under a good draught cupboard. The cinnabar is placed in a small flask and its own to twice the volume of chlorate of potassa is added, and then sufficient water to dissolve the greater part of the chlorate.

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* To thoroughly dry and purify the hydrogen evolved from zinc and dilute sulphuric acid, it should be passed through three wash-bottles, the first of which contains a solution of permanganate of potassa acidified with sulphuric acid, the second, a solution of potash or soda, and the last, pure concentrated sulphuric acid.

When this is done, about 25 c.c. of dilute hydrochloric acid is added gradually, with frequent agitation, and is left for 12 to 24 hours and finally warmed gently on the water-bath, when it dissolves completely without any separation of sulphur. Before precipitating by chloride of barium the sulphuric acid thus formed (§ 132, I. 1), the greater part of the free hydrochloric acid must be neutralised with ammonia and the liquid diluted to about 200 c.c.

b. Estimation of Mercury.—About 0·5 gram is dissolved as before, diluted, and allowed to stand in a moderately warm place until the odour of chlorine has almost disappeared; it is then filtered if necessary, ammonia added in excess, the whole heated gently for some time, hydrochloric acid added until the white precipitate of chloride of mercury and amide of mercury is redissolved, and from the solution, which measures about 400 c.c. and now no longer smells of chlorine, the mercury is precipitated as sulphide by means of sulphuretted hydrogen, as directed in § 118, 3.

Hg	100·00	86·21
S	16·00	13·79
	116·00	100·00

12. Crystallized Sulphide of Lime.

Clear and pure crystals of selenite are selected, ground to powder, and dried, if necessary, under the desiccator (§ 27).

a. Determination of Water.—From 1 to 2 grams is heated to low redness in a platinum or porcelain crucible, and the loss in weight determined. Compare § 35 *a* α and § 73 *a*.

b. Estimation of Sulphuric Acid and Lime.—About 1 gram is treated as in § 132, II. *b* α (Vol. I. p. 303). In order to get the fused mass out of the platinum crucible easily, it is left to cool completely, and then heated, without the lid, until the edge of the cake begins to melt, it is then again allowed to cool, sufficient water is poured into the crucible to cover the cake entirely, and the whole warmed slightly. The cake will at once become loose (Stöckmann).

CaO	28	32·56
SO_3	40	46·51
2aq	18	20·93
	86	100·00

C. Separation of Two Bases or Two Acids from each other, also Estimations in the Volumetric Way.

13. Separation of Iron from Manganese.

About 0·2 gram of fine pianoforte wire, and about the same quantity of ignited protosesquioxide of manganese (prepared as directed in § 109, 1, *a*), are dissolved in hydrochloric acid, heated with a little nitric acid, and the two metals, after diluting the solution to about 500 c.c., separated by means of acetate soda as in § 160, 3, *a* (**82**). The filtrate and washings are concentrated to about 200 c.c., and the manganese thrown down by carbonate of ammonia and weighed as manganosomanganic oxide (TAMM's method, § 160, 2, b. **81**). In the filtrate, concentrated by evaporation, any slight amount of manganese present is determined by bromine and ammonia (this vol. p. 525, top of page); any precipitate obtained in this way can at once be ignited and weighed as manganosomanganic oxide.

14. VOLUMETRIC ESTIMATIONS WITH POTASSIUM PERMANGANATE.

a. Standardizing the permanganate solution by metallic iron (fine piano wire), about 1 gram of which should be dissolved in dilute sulphuric acid (§ 112, 2 *a*, Vol. I. p. 215). It should be noted that it is better only to allow boiled distilled water to reascend into the boiling flask *a*, and not the water used as a seal, which frequently contains hydrocarbons.

b. Determination of the percentage content of oxalic acid.—From 1 to 2 grams of pure oxalic acid is weighed out, pressed between filter paper, dissolved in water, diluted to 250 c.c., and 50 c c. of it titrated as in § 112, 2 *a*, *α*, *cc*. (Vol. I. p. 217).

c. Determination of the amount of ferrous oxide in the ferrous ammonia sulphate.—12 grams of the pressed salt, dissolved in water with the addition of a little pure dilute hydrochloric acid, is diluted to 500 c.c, and the ferrous oxide is determined in 50 c.c.

α. In the solution of the salt acidified by sulphuric acid (Vol. I. p. 218 *β*).

β. In the solution acidified by hydrochloric acid; that is, after the addition of about 30 c.c. of hydrochloric acid of sp. gr. 1·2 (Vol. I. p. 219 *γ*).

γ. In the solution acidified by hydrochloric acid as in *β*, with the addition of 20 c.c. of a solution of protosulphate of manganese containing 200 grams of the salt per litre. By this addition, the disturbing influence of the hydrochloric acid is counteracted (F. KESSLER, Cl. ZIMMERMANN).

δ. In the solution acidified by hydrochloric acid as in *β*, with the addition of 10 to 20 c.c. of a cold saturated solution of chloride of lead (N. W. THOMAS).

FeO	36·00	18·36
NH_4O	26·04	13·28
$2SO_3$	80·00	40·81
6Aq	54·00	27·55
	196·04	100·00

15. VOLUMETRIC ESTIMATION OF IRON BY STANNOUS CHLORIDE.

About 5 grams of finely ground brown hæmatite (dried at 100° and subsequently heated to a moderate red heat) is warmed with strong hydrochloric acid until the ferric oxide is completely dissolved, a little chlorate of potassa is added if necessary, the whole heated until all the free chlorine is removed, diluted, filtered, and the solution made up to 250 or 500 c.c. and mixed by shaking.

The iron is estimated in 50 or 100 c.c. by means of stannous chloride according to § 113, 3. *b*, *a* (Vol. I. p. 225).

16. ESTIMATION OF NITRIC ACID IN NITRATE OF POTASSA.

a. Pure nitrate of potassa is heated, not to fusion, and transferred to a dry, well closed tube.

The nitric acid in 0·2 to 0·3 gram is estimated as directed in § 149, II., *d*, *β* (Vol. I. p. 394).

KO	47·13	46·58
NO_5	54·04	53·42
	101·17	100·00

b. As a control, an estimation of the nitric acid may be made as in § 149, II., *a*, *β*, by ignition with powdered quartz; comp. also § 320.

17. SEPARATION OF MAGNESIA FROM SODA.

About 0·2 gram of pure freshly calcined magnesia (which is easily obtained by igniting pure oxalate of magnesia, but which should, for safety, be washed with boiling water and re-calcined) and about 0·3 gram of pure, well dried chloride of sodium are weighed out and dissolved in dilute hydrochloric acid, avoiding too great excess, and separated by phosphate of ammonia (§ 153, B, 4, b, Vol. I. p. 416). As it is important that the latter should be added in slight excess only, a solution of known content is employed, and the amount to be added is calculated. The phosphoric acid is removed from the filtrate by means of ferric chloride (Vol. I. p. 416, *b. a*).

18. SEPARATION OF POTASH FROM SODA.

Powdered crystallized tartrate of potassa and soda (Rochelle salt) is pressed between blotting paper, about 1·5 grams weighed out, and heated in a platinum crucible, gradually at first, and then for some time to gentle ignition. The carbonaceous residue is completely extracted with water, and the residue, after being collected and washed, is carefully ignited, and again extracted with water. The united alkaline filtrates are acidified with hydrochloric acid, evaporated in a weighed platinum dish, and the chlorides of the alkali metals weighed together (§ 97, 3). The potassa and soda are then separated by bichloride of platinum (§ 152, *a*, and this vol. pp. 220 and 552); the potassium platinochloride is weighed, and the soda calculated from the difference.

KO	47·13	16·70
NaO	31·04	11·00
$C_8H_4O_{10}$	132·00	46·78
8aq	72·00	25·52
	282·17	100·00

19. VOLUMETRIC ESTIMATION OF CHLORINE IN METALLIC CHLORIDES AND THE INDIRECT DETERMINATION OF THE POTASSA AND SODA IN ROCHELLE SALT.

a. Preparation and examination of the nitrate of silver solution (§ 141, I. *b*. *a*, Vol. I. p. 355).

b. Indirect determination of the soda and potassa in Rochelle salt by volumetric estimation of the chlorine in the alkali chlorides obtained as in number 18. (For the calculation, see § 200, *a*, this vol. p. 98.)

20. ACIDIMETRY.

a. Preparation of normal hydrochloric acid, and of solution of soda (§ 215, I. and this vol. p. 191).

b. Testing the correctness of the normal hydrochloric acid with pure carbonate of soda, and with Iceland spar (§ 215, II., this vol. p. 193).

c. Preparation from normal sulphuric acid by means of normal caustic soda, known to be correct.

d. Determination of the strength of a diluted sulphuric acid by its specific gravity—*a* by means of the pyknometer (§ 209 *a*, this vol. p. 150, or § 278, this vol. p. 483); *b* by the areometer; and *c* by MOHR's balance (Zeitschr. f. anal. Chem. 9, 233). For the calculation see § 214, I. *a*, this vol. p. 181.

e. Determination of the strength of the same dilute sulphuric acid by normal caustic soda (§ 215 III. *a*, this vol. p. 194), using various indicators (§ 215, 6, this vol. pp. 198–200). See also THOMSON (Zeitschr. f. anal. Chem. 24, 222).

f. Determination of the strength of vinegar (§ 215, III. *a* and *b*, 3, this vol. pp. 194 and 196). In the case of white or slightly coloured vinegar, phenolphtalein is specially to be recommended as an indicator.

g. Estimation of the total tartaric acid in cream of tartar, according to the method of GOLDENBERG, GEROMENT & Co. (Zeitschr. f. anal. Chem. 22, 270). Exactly 3 grams of the finely powdered substance is heated to boiling for 10 to 20 minutes with 30 to 40 c.c. of water, and 2 to 2·5 grams of carbonate of potassa, stirring frequently; after cooling the solution somewhat (which will now contain all the tartaric acid in the form of neutral tartrate of potassa), it is transferred to a 100 c.c. measuring flask or cylinder, and allowed to cool completely. The flask or cylinder is then filled up to the mark, shaken up, and, after a time, filtered through a dry filter into a dry flask; 50 c.c. of the filtrate is now evaporated to 10 c.c., mixed with 2 c.c. of glacial acetic acid, in order to convert the neutral tartrate of potassa into acid tartrate of potassa, and 100–120 c.c. of alcohol, of 95 per cent. (at least), is added; the mixture is stirred well, and filtered after being left for a short time. The precipitate is washed with 95 per cent. alcohol until the washings, after dilution with water, no longer have an acid reaction; the still moist precipitate, together with the filter, is then put back into the porcelain basin and heated to boiling with water, stirring meanwhile. The liquid is now titrated with normal caustic soda, using litmus tincture or phenolphtalein. The number of c.c. required, when multiplied by 10, gives at once the percentage of hydrated tartaric acid in the substance examined, as it relates to 1·5 or the amount corresponding with 2/100 equiv. of hydrated tartaric acid which in the form of cream of tartar requires 10 c.c. of normal caustic soda. If the tartar is so impure that the precipitated tartrate is not white, a sensitive pale red litmus paper must be used to ascertain the completion of the titration (this vol. p. 196, 3). When this has to be done, it is requisite, in order to obtain perfectly accurate results, to test the caustic soda in the same manner, using the same litmus paper and chemically pure acid tartrate of potassa dried at 100°, as the standard fixed in this way differs slightly from that obtained by normal acid or by cream of tartar when tincture of litmus is employed.

h. Estimation of the acid tartrate of potassa in crude tartar.

The following exercise may be worked out either in place of, or in addition to, that given in *g*—that is, the pure tartar may be determined in a crude tartar or in wine yeast, by F. KLEIN'S* method.

The degree of acidity (this vol. p. 196, 3) is first obtained in the finely powdered and uniformly mixed substance, and from this the approximate amount of the tartar is calculated. As much of it as will contain 1·8 to 2·2 grams of acid tartrate of potassa is then weighed out, boiled up repeatedly with water (about five times), decanting each time through a filter; finally the residue is brought on to the filter and washed with boiling water until the washings no longer redden the litmus paper in the slightest degree. The united extracts are now evaporated down to 40 c.c., 5 grams of chloride of potassium is added, and the mixture stirred briskly with a glass rod for 15 minutes. For washing the now completely precipitated tartar, a solution is prepared by placing five grams of finely powdered pure tartar in a 250 c.c. flask with 200 c.c. of distilled water, and adding, after shaking, 25 grams of chloride of potassium, filling the flask up to the mark with distilled water, leaving it for a few hours, during which time it is frequently shaken, and finally filtering. A filter is now moistened with this liquid, the precipitated tartar is transferred to it, and, after completely draining, it is washed by dropping on to it the solution just mentioned, using 15 c.c. altogether; it is then allowed to drain completely once more, the precipitate and filter are put back into the basin, heated with water, and the tartar determined with N/2 caustic soda.† KLEIN recommends phenolphtalein as indicator. If the impure nature of the precipitated tartar necessitates the use of litmus paper in titrating, then the N/2 caustic soda must be standardised with pure cream of tartar dried at 100°, using the same litmus paper (see at the end of *g*).

21. ALKALIMETRY.

a. Preparation of the test acid according to the directions of DESCROIZILLES and GAY-LUSSAC (§ 219).

b. Valuation of a commercial potash, after expelling the water by gentle ignition as in § 224, III. 1 (this vol. p. 217).

- *α.* After MOHR (§ 220).
- *β.* After DESCROIZILLES and GAY-LUSSAC (§ 219).

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* Zeitschr. f. anal. Chem. 24, 383.

† As the 40 c.c. of filtrate contains a small quantity of tartar, a correction must be made; according to the author's experience an extra 0·2 c.c. of N/2 soda should be reckoned for 40 c.c. of the filtrate.

22. Estimation of Ammonia.

About 0·8 gram of pure (unsublimed) and dry chloride of ammonium is treated as directed in § 99, 3, *a* (Vol. I. p. 178).

NH_4Cl	18·04	33·72	NH_3	17·04	31·85
Cl	35·46	66·28	HCl	36·46	68·15
	53·50	100·00		53·50	100·00

23. Separation of Iodine from Chlorine.

About 0·8 gram of pure iodide of potassium, dried at 180° (§ 65, 6), and from 2 to 3 grams of pure dried chloride of sodium are dissolved and made up to 250 c.c., and the iodine and chlorine determined:

a. In 50 c.c., after § 169, 2, *b* (**263**). Calculation § 200, *c*.

b. In 10 c.c., after § 169, 2, *c* (**264**).

D. Analysis of Alloys, Minerals, Industrial Products, etc., by Gravimetric and Volumetric Methods.

24. Analysis of Brass.

This is carried out:

a. According to § 264, first method (this vol. p. 413).

b. Partly by electrolysis.

α. As a preliminary exercise about 2 grams of pure pressed sulphate of copper is dissolved, made up to 250 c.c., and the copper in 50 c.c. determined by electrolysis. For that purpose, 20 c.c. of nitric acid of sp. gr. 1·2 and 130 c.c. of water are added (this vol. p. 391), and the copper thrown down by means of an electric current (this vol. p. 391).

β. About 1·5 grams of brass is dissolved in nitric acid, the tin and lead removed as in *a*, the solution from which these have been separated is made up to 250 c.c., and the copper thrown down from 50 c.c. as in this vol. p. 391, after adding 20 c.c. of nitric acid of sp. gr. 1·2 and 130 c.c. of water. By means of a suitable aspirator,* the solution is first drawn off into a flask, without interrupting the current, and then the washings, the whole concentrated to about 100 c.c. by evaporation, and the zinc precipitated as in *a*.

25. Estimation of Silver in a Silver Coin.

A silver coin (" 20-Pfennigstück") is dissolved in 16 to 20 c.c. of nitric acid of sp. gr. 1·2 with the addition of a little water, and heated until all the nitrous acid is driven off; it is then diluted to 100 c.c., and the silver in 50 c.c. determined volumetrically by Volhard's method (this vol. p. 362).

26. Analysis of Soft Solder (Tin and Lead).

According to § 267, C. II. first method (this vol. p. 432).

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* See for example H. Fresenius and F. Bergmann, Zeitschr. f. anal. Chem. 19, 316.

27. ANALYSIS OF A DOLOMITE.

See § 235.

28. ANALYSIS OF A FELSPAR.

a. Decomposition by carbonate of soda (§ 140, II. *b*, *a*); removal of the silicic acid, which is weighed and then volatilised by hydrochloric acid to ascertain whether the silicic acid (Vol. I. p. 348, 2nd paragraph) contains any alumina; precipitation of the alumina together with the small quantity of ferric oxide by ammonia as in § 161, 4 (**115**); separation of the baryta from the filtrate by dilute sulphuric acid, and then of any lime that may be present by oxalate of ammonia, and any magnesia by phosphate of soda and ammonia, § 154, 6 (**36**). Finally the alumina is tested for silicic acid by fusing it with acid sulphate of potassa, and the ferric oxide present in the solution is determined as in § 160, 2 (**77**).

b. Decomposition by hydrochloric acid, preferably by AL. MITSCHERLICH's method (Vol. I. p. 351). It is then evaporated, with the addition of a little sulphuric acid, until no more hydrofluoric acid is evolved, finally heating more strongly until the greater part of the free sulphuric acid is also driven off; the residue is then treated with water, heated, and chloride of barium added carefully so long as a precipitate is formed, and when cold, but without previous filtration, carbonate of ammonia and ammonia are added. After being allowed to settle in the cold, it is filtered, the filtrate evaporated to dryness, and the residue ignited to drive off the ammonia salts. It is then dissolved in water, and any magnesia present, as also the small quantities of baryta and lime, are removed, as in this vol. p. 268, *e;* finally the potassa is estimated according to § 97, 3. If soda is also present, the alkalies must be separated as in § 152 (1). Where great accuracy is required, the small amount of potassa salt precipitated along with the sulphate of baryta must be taken into account, see this vol. p. 588.

29. ANALYSIS OF ZINC BLENDE.

a. Complete analysis.—The estimation of the sulphur, as well as the dissolution and the removal of any lead and other metals of the fifth or sixth groups which may be found, is carried out as in § 241, first method (this vol. p. 276), after which the process is as follows: The filtrate is heated to remove sulphuretted hydrogen, nitric acid is added, and the heating continued in order to convert the ferrous into ferric oxide, and, when cold, ammonia is added in excess. It is then filtered, washed, the precipitate dissolved in hydrochloric acid, and the ferric oxide and any alumina thrown down as basic salt, as in § 160, 3, *a* (**82**). The filtrate thus obtained is concentrated by evaporation, and ammonia added in slight excess to remove any remaining alumina and ferric oxide, the whole filtered if necessary, and (in case the precipitate is considerable) the precipitate by ammonia is repeated after dissolving the precipitate in hydrochloric acid. The precipitate is dissolved in hydrochloric acid, the solution mixed with the hydrochloric solution of the main precipitate of ferric oxide, precipitated with ammonia, and the washed precipitate dried, ignited, and weighed. It is then dissolved in concentrated hydrochloric acid, and any silica remaining undissolved determined and deducted from the weight found. If the solution thus obtained also contains alumina, the ferric oxide and alumina are separated as in § 160, 2 (**77**).

The united ammoniacal filtrates, which contain the whole of the zinc, are acidified by acetic acid, acetate of ammonia is added, and precipitation effected by sulphuretted hydrogen with the aid of heat. The sulphide of zinc is thoroughly washed with hot water containing some nitrate of ammonia, first by decantation, and finally on the filter, and the zinc estimated as in § 108, 2. The filtrate from the sulphide of zinc is highly concentrated by evaporation, bromine is added, then ammonia, and the whole heated. If a precipitate of hydrated peroxide of manganese is formed, it is collected, washed, dried, ignited, and the manganosomanganic oxide weighed. As small quantities of sulphide of manganese are occasionally thrown down along with the sulphide of zinc, it is necessary, as a precaution, to dissolve the weighed sulphide of zinc in hydrochloric acid with the addition of a little nitric acid, add bromine to the solution, then ammonia, and to ascertain whether, on digestion at a gentle heat, flakes of hydrated peroxide of manganese separate; if this happens, the manganese should be determined as above and taken into account in the calculation.

b. Volumetric estimation of the Zinc according to § 242.

30. ANALYSIS OF GALENA.

a. Estimation of the sulphur, lead, iron, &c., § 259, A, 1 (this vol. p. 363).

b. Estimation of the silver in galena after § 259, A, 3, *b* (this vol. p. 366).

31. VALUATION OF CHLORIDE OF LIME (§ 233, this vol. p. 241).

a. After PENOT (this vol. p. 243).

b. By an iodimetric method (this vol. p. 248). The preparation of the solutions required in *b*, and the determination of the liberated iodine, should be carried out as in § 146.

In order to obtain concordant results in the use of both methods, all the preparations must first be carefully made, so that the examination of the same milk of "chloride of lime" can be carried out by the methods *a* and *b* quickly.

32. VALUATION OF MANGANESE (§ 247).

a. Method of FRESENIUS and WILL (this vol. p. 291).
b. BUNSEN'S method (this vol. p. 296).

33. ESTIMATION OF SULPHUR IN PYRITES.

a. Estimation in the dry way (§ 256, II. 1, this vol. p. 356).
b. Estimation in the wet way (§ 256, II. 2, *b*, this vol. p. 358).

34. ESTIMATION OF ARSENIC IN AN IRON OCHRE OR IN AN OCHREOUS SEDIMENT FROM A FERRUGINOUS MINERAL WATER.

About 10 to 20 grams is digested with 50 to 100 c.c. of pure fuming hydrochloric acid, and the solution treated according to § 268, this vol. p. 438. If the receiver is connected with the condenser in such a manner as to be air-tight (as shown in fig. 78, Vol. I. 179), and a little water is placed in the receiver and in the Péligot tube connected with it, the hydrochloric acid solution mixed with excess of ferrous chloride solution can be at once distilled without previously diluting it with water, the process being thereby greatly facilitated.

35. ANALYSIS OF GUNPOWDER.

As described in § 227.

36. ESTIMATION OF CHROMIUM IN CHROME IRON ORE.

According to § 239, I., *a*, *b* or *c*, and II. *b*, *β*. In titrating the excess of ferrous oxide with permanganate of potassa, care must be taken to add sulphate of manganese (see Exercise 14, *c*. *γ*, p. 615).

37. ESTIMATION OF MANGANESE IN A MANGANESE ORE.

According to § 250.

38. ANALYSIS OF A CLAY OR A SOIL.

a. Mechanical analysis, according to § 238, I., or § 293 respectively.
b. Chemical analysis, according to § 238, II., or § 296 respectively.

39. ESTIMATION OF NICKEL AND COBALT IN AN ORE.

According to § 251, first method.

40. ESTIMATION IN PIG IRON OF THE CHEMICALLY COMBINED CARBON, GRAPHITE, SULPHUR, PHOSPHORUS, SILICON, AND ANY OTHER CONSTITUENTS WHICH MAY BE PRESENT.

According to § 255.

41. ANALYSIS OF A SPRING WATER OR A MINERAL WATER.

According to § 205 or § 206, *et seq.* respectively.

42. ANALYSIS OF THE ASH OF A PLANT.

According to § 283–290.

43. ESTIMATION OF THE SUGAR IN FRUIT, HONEY, MILK, OR THE LIKE.

According to § 274–277.

44. ESTIMATION OF ANTHRACENE IN A CRUDE ANTHRACENE.

According to § 282.

45. ESTIMATION OF ALCOHOL IN WINE OR IN ANY OTHER LIQUID CONTAINING ALCOHOL.

According to § 278.

46. ESTIMATION OF TANNIC ACID IN TANNING MATERIALS.

According to § 279.

E. Determination of the Solubility of Salts.

47. Determination of the Solubility of Common Salt.

a. At boiling heat.—Perfectly pure, pulverized chloride of sodium is dissolved in distilled water in a flask, heated to boiling, and kept in ebullition until part of the dissolved salt has separated. The liquid is now filtered as rapidly as possible, through a funnel surrounded with boiling water and covered with a glass plate, into an accurately weighed, capacious, measuring flask. As soon as about 100 c.c. of the solution has passed into the flask, it is closed with a cork, allowed to cool, and weighed. The flask is now filled up to the mark with water, and the salt in an aliquot portion of the liquid is determined by evaporating it in a platinum dish (best with the addition of some chloride of ammonium, which will, in some measure, prevent decrepitation on ignition), or by determining the chlorine (§ 141).

b. At 14°.—The boiling saturated solution is allowed to cool down to this temperature, shaking frequently, and then treated as in *a*.

100 parts of water dissolve at 109·7° . 40·35 of chloride of sodium.
100 „ „ 14° . 35·87 „ „

48. Determination of the Degree of Solubility of Sulphate of Lime.

a. At 100°.
b. At 18°.

Compare Marignac, Zeitschr. f. anal. Chem. 13, 57.

F. Determination of the Solubility of Gases in Liquids, and Analysis of Gaseous Mixtures.

49. Determination of the Absorption Coefficient of Sulphurous Acid.

See Ann. d. Chem. u. Pharm., vol. 95, page 1; also § 131, 2.

50. Analysis of Atmospheric Air.

That is the determination of the amount of carbonic acid (§ 336 to § 339), and oxygen (§ 341).

G. Organic Analysis, and Determinations of the Equivalents of Organic Compounds; also Analyses in which Organic Analysis has to be employed.

51. Analysis of Tartaric Acid.

Pure and colourless crystals are selected; these are powdered and dried at 100°.

a. It is burnt with oxide of copper, by v. Liebig's process (§ 174).
b. It is burnt with oxide of copper by Bunsen's process (§ 175).
c. It is burnt in oxygen (§ 178).

8C	48	32
6H	6	4
12O	96	64
	150	100

52. Estimation of the Nitrogen in Crystallized Ferrocyanide of Potassium.

The pure crystals are powdered, and the powder, if necessary, is pressed between blotting paper, and the nitrogen determined.

a. By Varrentrapp and Will's method (§ 186).

b. By Péligot's modification of Varrentrapp and Will's method (§ 187).

c. By Wilfarth's modification of Kjeldahl's process (§ 326).

53. Analysis of Uric Acid (or any other pure organic compound of carbon, hydrogen, oxygen, and nitrogen).

Pure uric acid is dried at 100°.

a. The carbon and hydrogen is determined (§ 183).

b. The nitrogen is determined.

  α. According to § 187.

  β. By Kjeldahl's process, Wilfarth's modification (§ 326).

  γ. By Dumas' method (§ 185).

5C	30·00	35·68
2N	28·08	33·40
2H	2·00	2·38
3O	24·00	28·54
	84·08	100·00

54. Analysis of Ether.

The portion employed must have been rendered anhydrous by digestion with fused chloride of calcium, and recently rectified. Process § 180.

8C	48	64·87
10H	10	13·51
2O	16	21·62
	74	100·00

55. Analysis of a Hard Coal.

According to § 272, B, this vol. 454.

The estimation of nitrogen is best effected by Wilfarth's modification of Kjeldahl's method (§ 326).

56. Analysis of a Bone-meal.

According to § 330, *a.*

57. Analysis of a Manure Mixture in which the Nitrogen is present in the form of Ammonia, Nitric Acid, and in Organic Combination, and the Phosphoric Acid is in different degrees of solubility.

According to § 333.

58. ANALYSIS OF BENZOIC ACID, AND DETERMINATION OF ITS EQUIVALENT.

a. The silver in benzoate of silver is determined as directed in § 115, 1 or 4.

b. The carbon and hydrogen in benzoic acid dried at 100°, is determined by any suitable method. Calculation, § 203, 2.

59. ANALYSIS OF AN ORGANIC BASE, AND DETERMINATION OF ITS EQUIVALENT.

Analysis of the base and its double salt with platinum. Calculation, § 203, 3.

60. DETERMINATION OF THE DENSITY OF CAMPHOR VAPOUR

Method described in § 194. Calculation, § 204.

APPENDIX.

I. ANALYTICAL NOTES.

1. *Action of Water on Glass and Porcelain Vessels, in the Process of Evaporation* (*to* § 41).

A large bottle was filled with water which had been cautiously distilled from a copper boiler with a tin condensing tube. All the experiments in 1 were made with this water.

a. 300 c.c., when cautiously evaporated in a platinum dish, left a residue weighing, after ignition, 0·0005 gram = 0·0017 per 1000.

b. 600 c.c. was evaporated in a wide flask of Bohemian glass, nearly to dryness, by boiling; the residue was transferred to a platinum dish, and the flask rinsed with 100 c.c. distilled water, which was added to the residue in the dish. After evaporating and igniting

The residue weighed	0·0104	gram
Deducting from this the quantity of fixed matter originally contained in the distilled water, namely	0·0012	,,
There remains substance taken up from the glass	0·0092	,,

= 0·0153 per 1000.

Three other experiments were made in the same manner, 300 c.c. left, in two, 0·0049 gram, and in the third 0·0037 gram; which, calculated for 600 c.c.

gives an average of	0·0090	gram
And after a deduction of	0·0012	,,
	0·0078	,,

= 0·013 per 1000.

We may therefore assume that 1 litre of water, when boiled down to a small bulk in glass vessels, dissolves about 14 milligrams of the constituents of the glass.

c. 600 c.c. was evaporated nearly to dryness in a dish of Berlin porcelain, and in all other respects treated as in *b.*

The residue weighed	0·0015	gram
Deducting from this the quantity of fixed matter contained in the distilled water, namely	0·0012	,,
There remains substance taken up from the porcelain	0·0003	,,

= 0·0005 per 1000.

2. *Action of Hydrochloric Acid on Glass and Porcelain Vessels, in the Process of Evaporation* (*to* § 41).

The distilled water used in 1 was mixed with 1/10th of pure hydrochloric acid.

a. 300 grams, evaporated in a platinum dish, left 0·002 grams of residue.

b. 300 grams, evaporated first in Bohemian glass nearly to dryness, then in a platinum dish, left 0·0019 residue; the dilute hydrochloric acid, therefore, had not attacked the glass.

c. 300 grams, evaporated in Berlin porcelain, &c., left 0·0036 gram accordingly, after deducting 0·002, 0·0016 = 0·0053 per 1000.

d. In a second experiment, made in the same manner as in *c.*, the residue amounted to 0·0034, accordingly, after deducting 0·002, 0·0014 = 0·0047 per 1000.

Hydrochloric acid, therefore, attacks glass much less than water. This shows that the action of water on glass consists in the formation of soluble basic silicates. Porcelain is much more attacked by water containing hydrochloric acid, than by pure water.

3. *Action of Solution of Chloride of Ammonium on Glass and Porcelain Vessels, in the Process of Evaporation* (*to* § 41).

In the distilled water of 1, 1/10th of chloride of ammonium was dissolved, and the solution filtered.

a. 300 c.c. evaporated in a platinum dish, left 0·006 gram of fixed residue.

b. 300 c.c., evaporated, first nearly to dryness in Bohemian glass, and then to dryness in a platinum dish, left 0·0179 gram ; deducting from this 0·006 gram, there remains substance taken up from the glass, 0·0119 = 0·0397 per 1000.

c. 300 c.c., treated in the same manner in Berlin porcelain, left 0·0178 ; deducting from this 0·006, there remains 0·0118 = 0·0393 per 1000.

Solution of chloride of ammonium, therefore, strongly attacks both glass and porcelain in the process of evaporation.

4. *Action of Solution of Carbonate of Soda on Glass and Porcelain Vessels* (*to* § 41).

In the distilled water of 1, 1/10th of pure crystallized carbonate of soda was dissolved.

a. 300 c.c., supersaturated with hydrochloric acid and evaporated to dryness in a platinum dish, &c., gave 0·0026 gram of silicic acid = 0·0087 per 1000.

b. 300 c.c. was gently boiled for three hours in a glass vessel ; the tolerably concentrated liquid, when treated as in *a*, left a residue weighing 0·1376 gram ; deducting from this the 0·0026 gram, left in *a*, there remains 0·135 gram = 0·450 per 1000.

c. 300 c.c., treated in the same manner as in *b*, in a porcelain vessel, left 0·0099 ; deducting from this 0·0026 gram, there remains 0·0073 = 0·0243 per 1000.

This shows that boiling solution of carbonate of soda attacks glass very strongly, and porcelain also in a very marked manner.

5. *Water distilled from Glass Vessels* (*to* § 56, 1).

42·41 grams of water distilled with extreme caution from a tall flask with a LIEBIG'S condenser, left, on evaporation in a platinum dish, a residue weighing, after ignition, 0·0018 gram, consequently $\frac{1}{23561}$.

6. *Sulphate of Potassa and Alcohol* (*to* § 68, *a*).

a. Pure ignited sulphate of potassa, when digested cold with absolute alcohol, for several days, with frequent shaking, gave a filtrate which, when diluted with water, and then mixed with chloride of barium, remained perfectly clear at first, and only began to show signs of a slight opalescence after the lapse of a considerable time. On evaporation to dryness, there remained a very slight residue, which gave, however, distinct indications of the presence of sulphuric acid.

b. The same salt treated in the same manner, with the addition of some pure concentrated sulphuric acid, gave a filtrate which, on evaporation in a platinum dish, left a clearly perceptible fixed residue of sulphate of potassa.

7. *Behaviour of Chloride of Potassium in the Air and at a High Temperature* (*to* § 68, *c*).

0·9727 gram of pure ignited (not fused) chloride of potassium, heated for 10 minutes to dull redness in an open platinum dish, lost 0·0007 gram ; the salt was then kept for 10 minutes longer at the same temperature, but no further diminution of weight was oberved. Heated to bright redness and semi-fusion, the salt suffered a further loss of weight to the extent of 0·0009 gram ; and when ignited intensely, until completely fused, it lost 0·0034 gram more. Eighteen hours' exposure to the air produced not the slightest increase of weight.

8. *Solubility of Potassium Platinochloride in Alcohol* (*to* § 68, *d*).

a. In absence of free Hydrochloric Acid.

α. An excess of perfectly pure, recently precipitated potassium platinochloride was digested for 6 days at 15—20°, with alcohol of 97·5 per cent., in a stoppered bottle, with frequent shaking. 72·5 grams of the perfectly colourless filtrate, on evaporation in a platinum dish, left a residue which, when dried at 100°, weighed 0·006 gram ; 1 part of the platinochloride requires therefore 12083 parts of alcohol for solution.

β. The same experiment was made with spirit of wine of 76 per cent. The filtrate might be said to be colourless, but on evaporation it blackened slightly, and the residue, therefore, was determined as platinum. 75·5 grams yielded 0·008 gram of platinum, corresponding with 0·02 gram of the double salt. One part of the salt dissolves accordingly in 3775 parts of spirit of wine of 76 per cent.

γ. The same experiment was made with spirit of wine of 55 per cent. The filtrate was distinctly yellowish. 63·2 grams left 0·0241 gram of platinum, corresponding with 0·06 gram of the double salt. One part of the salt, therefore, dissolves in 1053 parts of spirit of wine of 55 per cent.

b. In presence of free Hydrochloric Acid.

Recently precipitated potassium platinochloride was digested cold with spirit of wine of 76 per cent., to which some hydrochloric acid had been added. The solution was yellowish ; 67 grams left 0·0146 gram of platinum, which corresponds with 0·0365 gram of potassium platinochloride. One part of the salt, therefore, dissolves in 1835 parts of spirit of wine, mixed with hydrochloric acid.

9. *Sulphate of Soda and Alcohol* (*to* § 69, *a*).

Experiments made with pure anhydrous sulphate of soda, in the manner described in 6, showed that this salt behaves both towards pure alcohol, and towards alcohol containing sulphuric acid, exactly like sulphate of potassa.

10. *Behaviour of ignited Sulphate of Soda on exposure to the Air* (*to* § 69, *a*).

2·5169 grams of anhydrous sulphate of soda on exposure, in a watch-glass, to the open air on a hot summer day, did not increase in weight during the first few minutes, but after the lapse of 5 hours there was an increase of 0·0061 gram

11. *Experiments with Nitrate of Soda* (*to* § 69, *b*).

a. 4·5479 grams of pure fused nitrate of soda on being exposed to the air (in April, in fine weather) for 24 hours, increased in weight 0·0006 gram.

b. 4·5479 grams of pure nitrate of soda was dissolved in water, in a platinum dish, and pure nitric acid added to the solution; the mixture was then evaporated to dryness on the water-bath, and the residue cautiously heated until the mass at the bottom of the dish began to fuse. The contents of the dish when cold weighed 4·5503 grams, and after being heated again to complete fusion, 4·5474 grams.

12. *Behaviour of Chloride of Sodium on exposure to the Air* (*to* § 69, *c*).

4·3281 grams of chemically pure, moderately ignited (not fused) chloride of sodium, which had been cooled under a bell-glass over sulphuric acid, on exposure for 45 minutes to the (somewhat moist) air, increased in weight 0·0009 gram.

13. *Behaviour of Chloride of Sodium when Ignited alone, and with Chloride of Ammonium* (*to* § 69, *c*).

4·3281 grams of chemically pure, ignited chloride of sodium was dissolved in water, in a moderate-sized platinum dish, pure chloride of ammonium was added to the solution, the whole evaporated, and the residue gently heated until there was no longer any apparent evolution of chloride of ammonium fumes. The residue weighed 4·3334 grams. After being very gently ignited for about 2 minutes, it weighed 4·3314 grams. Ignition for a short time at a red heat reduced the weight to 4·3275 grams, and after exposure for 2 minutes longer to a bright red heat (upon which occasion white fumes were seen to escape), to 4·3249 grams.

14. *Behaviour of Carbonate of Soda on exposure to the Air, and on Ignition* (*to* § 69, *d*).

2·1061 grams of moderately ignited, chemically pure carbonate of soda was exposed to the air in an open platinum dish, in July, in dull weather; after 10 minutes the weight was 2·1078, after 1 hour 2·1113, after 5 hours 2·1257 grams.

1·4212 grams of moderately ignited, chemically pure carbonate of soda, on being ignited for 5 minutes in a covered platinum crucible, but so that no fusion took place, weighed 1·4212 grams. After being heated more strongly for 5 minutes, so that it was partially fused, it weighed 1·4202, and after being fused for 5 minutes, 1·4135 grams.

15. *Behaviour of Chloride of Ammonium on Evaporation and Drying* (*to* § 70, *a*).

0·5625 gram of pure and thoroughly dry chloride of ammonium was dissolved in water in a platinum dish, evaporated to dryness on the water-bath, and completely dried in a water-oven; the weight was now found to be 0·5622 gram (ratio 100 : 99·94). After being again heated for 15 minutes in the water-oven, it weighed 0·5612 gram (ratio 100 : 99·77). Exposed once more for 15 minutes to the same temperature, it weighed 0·5608 gram (ratio 100 : 99·69).

16. *Solubility of Ammonium Platinochloride in Alcohol* (*to* § 70, *b*).

a. In absence of free Hydrochloric Acid.

α. An excess of perfectly pure, recently precipitated ammonium platinochloride was digested for 6 days, at 15—20°, with alcohol of 97·5 per cent., in a stoppered bottle, with frequent agitation.

74·3 grams of the perfectly colourless filtrate, on evaporation and ignition in a platinum dish, left 0·0012 gram of platinum, corresponding with 0·0028 of the salt; 1 part of the salt requires accordingly 26535 parts of alcohol of 97·5 per cent.

β. The same experiment was made with spirit of wine of 76 per cent. The filtrate was distinctly yellowish.

81·75 grams left 0·0257 gram of platinum, which corresponds with 0·0584 gram of the salt; 1 part of the salt dissolves accordingly in 1406 parts of spirit of wine of 76 per cent.

γ. The same experiment was made with spirit of wine of 55 per cent. The filtrate was distinctly yellow. Slight blackening ensued on evaporation, and 56·5 grams left 0·0364 gram of platinum, which corresponds with 0·08272 gram of the salt. Consequently, 1 part of the salt dissolves in 665 parts of spirit of wine of 55 per cent.

b. In presence of Hydrochloric Acid.

The experiment described in *β* was repeated, with this modification, that some hydrochloric acid was added to the spirit of wine. 76·5 grams left 0·0501 gram of platinum, which corresponds with 0·1139 gram of the salt: therefore, 672 parts of the acidified spirit had dissolved 1 part of the salt.

17. *Solubility of Carbonate of Baryta in Water* (*to* § 71, *b*).

a. In Cold Water.—Perfectly pure, freshly precipitated BaO,CO_2 was digested for 5 days with water at 16—20°, shaking frequently. The filtrate immediately became turbid with sulphuric acid, but with ammonia, only after the lapse of a considerable time. 84·82 grams of the solution, on evaporation, left 0·0060 BaO,CO_2; consequently 1 part of that salt dissolves in 14137 parts of cold water.

b In Hot Water.—The same carbonate of baryta, when boiled for 10 minutes with pure distilled water, gave a filtrate having the same reactions as that prepared with cold water, and remaining perfectly clear on cooling. 84·82 grams of the hot solution, on evaporation, left 0·0055 gram of carbonate of baryta. One part of that salt dissolves, therefore, in 15421 parts of boiling water.

18. *Solubility of Carbonate of Baryta in Water containing Ammonia and Carbonate of Ammonia* (*to* § 71, *b*).

A solution of chemically pure chloride of barium was mixed with ammonia and carbonate of ammonia in excess, gently heated, and left for 12 hours: the filtrate remained perfectly clear on adding sulphuric acid, but after a long time, a scarcely perceptible precipitate separated. 84·82 grams of the filtrate, on evaporation in a small platinum dish and subsequent gentle ignition, left 0·0006 gram. 1 part of the salt, therefore, had dissolved in 141000 parts of the liquid.

19. *Solubility of Silicofluoride of Barium in Water* (*to* § 71, *c*).

a. Recently precipitated, thoroughly washed silicofluoride of barium was digested for 4 days in cold water, with frequent shaking; the filtrate, when tested with dilute sulphuric acid, at once became turbid, and also with sulphate of lime after 1 or 2 seconds, precipitates separating from both after the lapse of some time. 84·82 grams of the filtrate left a residue which after being thoroughly dried, weighed 0·0223 gram, 1 part of the salt requiring 3802 parts of cold water to dissolve it.

b. Another sample of freshly precipitated silicofluoride of barium was heated with water to boiling, and the solution allowed to cool (when some of the dissolved salt separated). The solution left for a considerable time in contact with the undissolved salt, behaved towards solution of sulphate of lime as in *a*. 84·82 grams of it left 0·025 gram; 1 part of the salt accordingly dissolved in 3392 parts of water.

20. *Solubility of Silicofluoride of Barium in Water acidified with Hydrochloric Acid* (*to* § 71, *c*).

a. Recently precipitated, pure silicofluoride of barium was digested during 3 weeks with cold water acidified with hydrochloric acid, agitating frequently. The filtrate gave a rather copious precipitate with sulphuric acid. 84·82 grams left 0·1155 gram of thoroughly dried residue, which, calculated as silicofluoride of barium, gives 1 part of that salt to 733 parts of liquid.

b. Recently precipitated, pure silicofluoride of barium was mixed with water very slightly acidified with hydrochloric acid, and heated to boiling. Cooled to 12°, 84·82 grams of the filtrate left a residue of 0·1322 gram, which gives 1 part of the salt to 640 parts of liquid.

N.B.—Silicofluoride of barium cannot be dissolved in hydrochloric acid without undergoing decomposition; at all events, the residue, even after ignition, contained a rather large proportion of chloride of barium.

21. *Solubility of Sulphate of Strontia in Water* (*to* § 72, *a*).

a In Water at 14°. 84·82 grams of a solution prepared by digesting recently precipitated sulphate of strontia with water during 4 days at the ordinary temperature, left 0·0123 gram of sulphate of strontia; or 1 part of SrO,SO_3 dissolves in 6895 parts of water.

b. In Water at 100°. 84·82 grams of a solution prepared by boiling recently precipitated sulphate of strontia several hours with water, left 0·0088 gram; or 1 part of SrO,SO_3 dissolves in 9638 parts of boiling water.

22. *Solubility of Sulphate of Strontia in Water containing Hydrochloric Acid and Sulphuric Acid* (*to* § 72, *a*).

a. 84·82 grams of a solution prepared by 3 days' digestion, left 0·0077 gram of SrO,SO_3.

b. 42·41 grams of a solution prepared by 4 days' digestion, left 0·0036 gram.

c. Pure carbonate of strontia was dissolved in an excess of hydrochloric acid, and the solution precipitated with an excess of sulphuric acid was left in the cold for a fortnight; 84·82 grams of the filtrate left 0·0066 gram.

In *a.* 1	part of SrO,SO_3	required	11016 parts.
b. 1	,,	,,	11780 ,,
c. 1	,,	,,	12791 ,,
	Mean	. .	11862 parts.

23. *Solubility of Sulphate of Strontia in dilute Nitric Acid, Hydrochloric Acid, and Acetic Acid* (*to* § 72, *a*).

a. Recently precipitated, pure sulphate of strontia was digested for 2 days in the cold with nitric acid of 4·8 per cent.; 150 grams of the filtrate left 0·3451 gram, so that 1 part of the salt dissolved in 435 parts of the dilute acid. In another experiment, 1 part of the salt was found to require 429 parts of the dilute acid. Mean, 432 parts.

b. The same salt was digested for 2 days in the cold with hydrochloric acid of 8·5 per cent.; 100 grams left 0·2115, and in another experiment, 0·2104 gram. 1 part of the salt, therefore, dissolves in 474 parts of hydrochloric acid of 8·5 per cent.

c. The same salt was digested for 2 days in the cold with acetic acid of 15·6 per cent. Ac,HO; 100 grams left 0·0126, and in another experiment, 0·0129 gram. 1 part of sulphate of strontia, therefore, in the mean, dissolves in 7843 parts of acetic acid of 15·6 per cent.

24. *Solubility of Carbonate of Strontia in Cold Water* (*to* § 72, *b*).

Recently precipitated, thoroughly washed SrO,CO_2 was digested for several days with cold distilled water, shaking frequently. 84·82 grams of the filtrate, on evaporation, left a residue weighing, after ignition, 0·0047 gram. 1 part of carbonate of strontia requires therefore 18045 parts of water to dissolve it.

25. *Solubility of Carbonate of Strontia in Water containing Ammonia and Carbonate of Ammonia* (*to* § 72, *b*).

Recently precipitated, thoroughly washed carbonate of strontia was digested for four weeks with cold water containing ammonia and carbonate of ammonia, shaking frequently. 84·82 grams of the filtrate left 0·0015 gram SrO,CO_2, consequently, 1 part of the salt dissolves in 56545 parts of the liquid.

If solution of chloride of strontium is precipitated with carbonate of ammonia and ammonia, as directed in § 102, 2, *a*, sulphuric acid produces no turbidity in the filtrate, after the addition of alcohol.

26. *Solubility of Carbonate of Lime in Water containing Ammonia and Carbonate of Ammonia* (*to* § 73, *b*).

Pure, dilute solution of chloride of calcium was precipitated with carbonate of ammonia and ammonia, allowed to remain 24 hours, and then filtered. 84·82 grams left 0·0013 gram CaO,CO_2, or 1 part requires 65246 parts to dissolve it.

27. *Behaviour of Carbonate of Lime on Ignition in a Platinum Crucible* (*to* § 73, *b*).

0·7955 gram of thoroughly dried carbonate of lime was exposed, in a small and thin platinum crucible, to the gradually increased, and finally most intense heat of a good BERZELIUS' lamp, the crucible being open and placed obliquely. After the first 15 minutes the mass weighed 0·6482—after half an hour 0·6256—after 1 hour 0·5927, the last weight remaining unaltered after 15 minutes additional heating. This corresponds with 74·5 per cent. (calculating 56·0 per cent. lime): the whole of the carbonic acid, therefore, was not driven off.

28. *Composition of Oxalate of Lime dried at* 100° (*to* § 73 *c*).

0·8510 gram of thoroughly dry, pure carbonate of lime was dissolved in hydrochloric acid, the solution precipitated with oxalate of ammonia and ammonia, and the precipitate collected upon a weighed filter and dried at 100° until the weight remained constant; the oxalate of lime so produced weighed 1·2461 gram. Calculating this as $CaO,C_2O_3+aq.$, the amount found contained 0·4772 CaO = 56·07 per cent. in the carbonate of lime; the calculated proportion of lime in the latter is 56·0 per cent.

29. *Behaviour of freshly Ignited Caustic Lime on exposure to the Air* (*to* § 73, *d*).

0·5599 gram of caustic lime, obtained by igniting oxalate of lime in a covered platinum crucible over the blowpipe, after standing in the scale pan 1 minute weighed 0·5599 gram ; after 2 minutes, 0·5605 ; after 6 minutes, 0·5609 ; after 17 minutes, 0·5625. The platinum crucible containing the caustic lime, was left for 15 minutes in the desiccator before making the first weighing.

30. *Behaviour of Sulphate of Magnesia in the Air and on Ignition* (*to* § 74, *a*).

0·8135 gram of perfectly pure anhydrous MgO,SO_3 kept for half an hour in a covered platinum crucible on a fine and warm day in June, increased in weight 0·004 gram, and in the course of 12 hours, 0·067 gram. In the open crucible, the salt could not be accurately weighed, owing to continual increase of weight.

0·8135 gram, exposed for some time to a very low red heat, suffered no diminution in weight ; but after 5 minutes exposure to an intense red heat, it lost 0·0075 gram, and the residue no longer gave a clear solution with water. About 0·2 gram of pure sulphate of magnesia exposed in a small platinum crucible, for 15 to 20 minutes, to the heat of a powerful blast gas-lamp, gave, with dilute hydrochloric acid, a solution in which chloride of barium did not produce the slightest turbidity.

31. *Solubility of Basic Phosphate of Magnesia and Ammonia in Pure Water* (*to* § 74, *b*).

a. Recently precipitated basic phosphate of magnesia and ammonia, after being thoroughly washed with water, was digested for 24 hours with water at at about 15°, shaking frequently.

84·82 grams of the filtrate left . . . . . 0·0047 gram of pyrophosphate of magnesia.

b. The same precipitate was digested in the same manner for 72 hours.

84·42 grams of the filtrate left . . . . . . 0·0043 „

Mean 0·0045 „

which corresponds with 0·00552 gram of the anhydrous double salt ; 1 part of that salt dissolves, therefore, in 15293 parts of pure water.

With ammonia, the cold, saturated solution, after the lapse of a short time, gave a distinctly crystalline precipitate ;—with phosphate of soda, it remained perfectly clear, and even after the lapse of two days no precipitate had formed ;—phosphate of soda and ammonia produced a precipitate apparently as large as that obtained with ammonia.

32. *Behaviour of Acid Solutions of Pyrophosphate of Magnesia towards Ammonia* (*to* § 74, *c*).

0·3985 gram of pyrophosphate of magnesia was heated, for several hours, with concentrated sulphuric acid ; this had no perceptible action, and it was only after some water had been added that the salt dissolved. On adding ammonia in excess to the solution after it had been heated for some time, it gave a crystalline precipitate, which was collected after 18 hours ; the quantity of pyrophosphate of magnesia obtained was 0·3805 gram, that is 95·48 per cent. In the filtrate, phosphate of soda produced a trifling precipitate, which gave 0·0150 gram of pyrophosphate of magnesia, that is, 3·76 per cent.

0·3565 gram of pyrophosphate of magnesia was dissolved in 3 grams of nitric acid, of sp. gr. 1·2, and the solution heated, diluted, and precipitated with ammonia. The quantity of pyrophosphate of magnesia obtained amounted to 0·3485 gram, that is, 98·42 per cent.: 0·4975 gram was treated in the same manner with 7·6 grams of the same nitric acid: the quantity re-obtained was 0·4935 gram, that is, 99·19 per cent.

0·786 gram treated in the same manner with 16·2 grams of nitric acid, gave 0·7765 gram, that is, 98·79 per cent.

The result of these experiments may be tabulated thus:

Proportion of $2MgO,PO_5$ to nitric acid.	Re-obtained.	Loss.
1 : 9	98·42 per cent.	1·58
1 : 15	99·19 „	0·81
1 : 20	98·79 „	1·21

33. *Solubility of Pure Magnesia in Water* (*to* § 74, *d*).

a. In Cold Water.—Perfectly pure, well crystallised sulphate of magnesia was dissolved in water, the solution precipitated with carbonate of ammonia and caustic ammonia, and the precipitate thoroughly washed, but in spite of this it still retained a perceptible trace of sulphuric acid. It was then dissolved in pure nitric acid, an excess of acid being carefully avoided, the solution again precipitated with carbonate of ammonia and caustic ammonia, and the precipitate thoroughly washed. The perfectly pure basic carbonate of magnesia thus prepared was ignited in a platinum crucible until the weight remained constant, and the residue of pure magnesia was then digested in the cold for 24 hours with distilled water, shaking frequently, the distilled water used being quite free from chlorine, and having no fixed residue on evaporation.

α. 84·82 grams of the filtrate, when cautiously evaporated in a platinum dish, left a residue weighing, after ignition, 0·0015 gram; 1 part of the pure magnesia dissolved therefore in . . . . 56546 parts of cold water.

The digestion was continued for 48 hours longer, when

β. 84·82 grams left 0·0016 gram. 1 part required, therefore . 53012

γ. 84·82 grams left 0·0015 gram. 1 part required . . . 56546

Average 55368

The solution of magnesia prepared in the cold has a feeble yet distinct alkaline reaction, which is most easily perceived on adding very faintly reddened tincture of litmus; the alkaline reaction of the solution is perfectly manifest also with slightly reddened litmus paper, or turmeric or dahlia paper, if these test-papers are left for some time in contact with the solution.

Alkali carbonates fail to render the solution turbid, even on boiling.

It also remains clear with phosphate of soda, but if ammonia is added, it soon becomes turbid on shaking, and after some time deposits a perceptible precipitate of basic phosphate of magnesia and ammonia.

b. In Hot Water.—On boiling pure magnesia with water, a solution is obtained which behaves in every respect like the solution prepared in the cold. It does not become turbid on cooling, neither does a solution prepared in the cold become turbid on boiling. 84·82 grams of the solution prepared by boiling left 0·0016 gram MgO.

34. *Solubility of Pure Magnesia in Solutions of Chloride of Potassium and Chloride of Sodium* (*to* § 74, *d*).

Three flasks of equal size were charged as follows:

1. With 1 gram of pure chloride of potassium, 200 c.c. of water and some perfectly pure magnesia free from carbonate.
2. With 1 gram of pure chloride of sodium, 200 c.c. of water and some pure magnesia.

3. With 200 c.c. of water and some pure magnesia.

The contents of the 3 flasks were kept boiling for 40 minutes, then filtered, and the clear filtrates mixed with equal quantities of a mixture of phosphate of soda, chloride of ammonium and ammonia. After 12 hours, a very slight precipitate was visible in 3, but there was a considerably larger precipitate in 1 and 2.

35. *Precipitation of Alumina by Ammonia, etc.* (*to* § 75, *a*).

a. On adding ammonia to a neutral solution of a salt of alumina or of alum, a gelatinous precipitate of hydrate of alumina is produced, as is well known. On adding more ammonia, the precipitate gradually redissolves, but never entirely.

b. If a drop of a dilute solution of alum is added to a large amount of ammonia, the solution appears almost perfectly clear after shaking; after a considerable time, however, it deposits light flocks.

c. If a solution of alumina, mixed with a large amount of ammonia, is filtered, and

α. The filtrate boiled for a considerable time, flocks of hydrate of alumina separate gradually in proportion as the excess of ammonia escapes.

β. On mixing the filtrate with solution of chloride of ammonium, a very perceptible flocculent precipitate of hydrate of alumina separates immediately; the whole of the hydrated alumina present in the solution will thus separate if the chloride of ammonium be added in sufficient quantity.

γ. If the filtrate is mixed with sesquicarbonate of ammonia, the same reaction takes place as in β.

δ No precipitate separates on mixing the filtrate with solution of chloride of sodium or chloride of potassium, but, after several days, light flocks of hydrate of alumina subside, owing to the loss of ammonia by evaporation.

d. If a neutral solution of alumina is precipitated with carbonate of ammonia, or if a solution strongly acidified with hydrochloric or nitric acid is precipitated with pure ammonia, or if, to a neutral solution, a sufficient amount of chloride of ammonium is added besides the ammonia, the precipitants, even in considerable excess, will fail to redissolve the precipitated alumina, as appears from the fact that the filtrates remain perfectly clear even on protracted boiling and evaporation.

36. *Precipitation of Alumina by Sulphide of Ammonium* (*to* § 75, *a*).

(*Experiments made by Mr.* J. FUCHS, *formerly assistant in the author's laboratory.*)

a. 50 c.c. of a solution of pure ammonia alum, which contained 0·3939 gram of alumina, was mixed with 50 c.c. of water and 10 c.c. of a solution of sulphide of ammonium, and filtered after ten minutes. The ignited precipitate weighed 0·3825 gram.

b. The same experiment was repeated with 100 c.c. of water; the precipitate weighed 0·3759 gram.

c. The same experiment was repeated with 200 c.c. of water; the precipitate weighed 0·3642 gram.

37. *Precipitation of Sesquioxide of Chromium by Ammonia* (*to* § 76, *a*).

Solutions of sesquichloride of chromium and of chrome alum, concentrated or dilute, neutral or acidified with hydrochloric acid, were mixed with ammonia in excess; all the filtrates were red, but if boiled before being filtered they were all colourless, provided the ebullition had been sufficiently protracted.

38. *Solubility of Basic Carbonate of Zinc in Water* (*to* § 77, *a*).

Perfectly pure, recently (hot) precipitated basic carbonate of zinc was gently heated with distilled water, and subsequently digested in the cold for many weeks, shaking frequently. The clear solution gave not the slightest precipitate with sulphide of ammonium, even after long standing.

84·82 grams left 0·0014 gram of oxide of zinc, corresponding with 0·0019 of basic carbonate of zinc (74 per cent. of ZnO being assumed in this salt): 1 part, therefore, requires 44642 parts of water to dissolve it.

39. *Behaviour of Sulphide of Zinc when Washed* (*to* § 77, *c*).

In these experiments, as also in 40 and 41, the sulphide of the metal was precipitated from a solution of the neutral salt, containing chloride of ammonium, by adding to it yellow sulphide of ammonium and allowing it to remain in a closed vessel for 24 hours; first the clear liquid and then the precipitate was poured on to 6 filters of equal size, so that the amount of the metallic sulphide on each filter was about the same. The washing was at once commenced and continued, without interruption, the following liquids being used:

I. Pure water.
II. Water containing sulphuretted hydrogen.
III. Water containing sulphide of ammonium.
IV. Water containing chloride of ammonium, afterwards pure water.
V. Water containing sulphuretted hydrogen and chloride of ammonium, afterwards water containing sulphuretted hydrogen.
VI. Water containing sulphide of ammonium and chloride of ammonium, afterwards water containing sulphide of ammonium.

The filtrates were at first clear and colourless, but on washing, the first three filtrates ran through turbid, the turbidity being strongest in II. and weakest in III.; the last three filtrates remained quite clear. On adding sulphide of ammonium no change took place in any of them; the turbidity of the first three was not increased, and the clearness of the last three was not impaired. Chloride of ammonium therefore decidedly exercises a favourable action, and the water containing it may subsequently be displaced by water containing sulphide of ammonium.

40. *Behaviour of Sulphide of Manganese when Washed* (*to* § 78, *e*).

The filtrates, as in 39, were at first clear and colourless, but after the washing had been continued some time, I. appeared colourless, slightly opalescent; II. whitish and turbid; III. yellowish and turbid; IV. colourless, slightly turbid; V. slightly yellowish, nearly clear; VI. clear, yellowish. To obtain a filtrate that will remain clear, therefore, the wash-water must at first contain chloride of ammonium, but the addition of sulphide of ammonium cannot be dispensed with, as all the washings obtained without the use of it gave distinct precipitates of sulphide of manganese on adding some of the reagent.

41. *Behaviour of Sulphide of Nickel* (*also of Sulphide of Cobalt and Sulphide of Iron*) *when Washed* (*to* § 79, *e*).

In the experiments with sulphide of nickel, the clear filtrates were put aside, as in 39, and the washing then proceeded with. The washings of the first three ran through turbid, whilst the last three were clear. When the washing was finished, I. was colourless and clear, but became brown on adding sulphide of ammonium; II. was blackish and clear, and sulphide of ammonium produced no change; III. was dirty yellow and clear, and remained unaltered on the addition of the sulphide; IV. was colourless and clear, but was rendered black and opaque by sulphide of ammonium; V. was slightly opalescent, and became brown and clear with sulphide of ammonium; VI. was slightly brownish and opalescent, and on adding the sulphide became almost pure yellow and clear.

Sulphide of cobalt and sulphide of iron behaved in an exactly similar manner. It is evident that these sulphides oxidize more rapidly when the wash-water contains chloride of ammonium, unless sulphide of ammonium is also present. It is necessary, therefore, to wash with a liquid containing sulphide of ammonium, and the addition of chloride of ammonium at first is strongly recommended, as it diminishes the likelihood of a muddy filtrate being obtained.

42. *Solubility of Carbonate of Lead* (*to* § 83, *a*).

a. In pure Water.—Recently precipitated, and thoroughly washed, pure carbonate of lead was digested for 8 days with water, at the ordinary temperature, shaking frequently. 84·42 grams of the filtrate, to which some pure sulphuric acid was added, left 0·0019 gram of sulphate of lead on evaporation, which corresponds with 0·00167 of carbonate of lead, so that 1 part of the latter dissolves in 50551 parts of water. This solution, when mixed with sulphuretted hydrogen water, remained perfectly colourless, not the least tint being detected in it, even on looking through it from the top of the test cylinder.

b. In Water containing a little Acetate of Ammonia, and also Carbonate of Ammonia, and Ammonia.—A highly dilute solution of pure acetate of lead was mixed with carbonate of ammonia and ammonia in excess, the whole gently heated, and then allowed to remain several days; 84·42 grams of the filtrate, on evaporation with a little sulphuric acid, left 0·0041 gram of sulphate of lead, which corresponds with 0·0036 of the carbonate, so that 1 part of the latter requires 23450 parts of the above liquid to dissolve it. The solution, when mixed with sulphuretted hydrogen water, gave a distinct coloration on looking through it from the top of the test cylinder, but laterally this coloration was hardly perceptibly. Traces of sulphide of lead separated after the lapse of a long time.

c. In Water containing much Nitrate of Ammonia together with Carbonate of Ammonia and Caustic Ammonia.—To a highly dilute solution of acetate of lead, nitric acid was first added, then carbonate of ammonia and ammonia in excess, and the whole gently heated, and allowed to remain for 8 days. The filtrate, when mixed with sulphuretted hydrogen, exhibited a very distinct brownish colour on looking through it from the top of the cylinder, but appeared only very slightly coloured on looking through the cylinder laterally. The amount of lead dissolved was unquestionably somewhat more than in *b*.

43. *Solubility of Oxalate of Lead* (*to* § 83, *b*).

A dilute solution of acetate of lead was precipitated with oxalate of ammonia and ammonia, and left for some time. The filtrate, when mixed with sulphuretted hydrogen, behaved exactly like the filtrate of No. 42 *b*, that is the liquid appeared pale brown on looking through it from the top of the test cylinder, but viewed laterally was colourless. The same behaviour was observed in another similar experiment, in which nitrate of ammonia had been added to the solution.

44. *Solubility of Sulphate of Lead in Pure Water* (*to* § 83, *d*).

Thoroughly washed and still moist sulphate of lead was digested for 5 days with water, at 10—15°, shaking frequently. 84·42 grams of the filtrate (filtered off at 11°) left 0·0037 gram of sulphate of lead, so that 1 part of it requires 22816 parts of pure water at 11°.

The solution, when mixed with sulphuretted hydrogen, was distinctly brown when viewed from the top of the cylinder, but very slightly so when seen laterally.

45. *Solubility of Sulphate of Lead in Water containing Sulphuric Acid* (*to* § 83, *d*).

A very dilute solution of acetate of lead, mixed with an excess of dilute pure sulphuric acid, was very gently heated, and the precipitate allowed several days to subside. 80·31 grams of the filtrate left 0·0022 gram of sulphate of lead, so that 1 part of the salt requires 36504 parts of the acidified liquid to dissolve it. The solution, when mixed with sulphuretted hydrogen, appeared colourless to the eye looking through the cylinder laterally, and but very little darker when viewed from the top of the cylinder.

46. *Solubility of Sulphate of Lead in Water containing Ammoniacal Salts and free Sulphuric Acid* (*to* § 83, *d*).

A very dilute solution of acetate of lead was mixed with a rather large amount of nitrate of ammonia, and sulphuric acid added in excess. After several days, the mixture was filtered, and the filtrate was found to be nearly indifferent to sulphuretted hydrogen water; viewed from the top of the cylinder, it was hardly perceptibly darker than pure water.

47. *Behaviour of Sulphate of Lead when Ignited* (*to* § 83, *d*).

Speaking of the determination of the atomic weight of sulphur, ERDMANN and MARCHAND* state that sulphate of lead loses some sulphuric acid when ignited. In order to obtain information as to the extent of this loss, and to ascertain how far it might impair the accuracy of the method of determining lead as sulphate, the author heated 2·2151 grams of absolutely pure PbO,SO_3, to a most intense red heat, over a spirit lamp with double draught, but not the slightest decrease of weight could be observed; in no case did it amount to 0·0001 gram.

48. *Behaviour of Sulphide of Lead on Drying at* 100° (*to* § 83, *f*).

Sulphide of lead was precipitated from a solution of pure acetate of lead by sulphuretted hydrogen, and when dry, kept for a considerable time at 100° and weighed occasionally. The following numbers represent the results of 5 weighings: I. 0·8154; II. 0·8164; III. 0·8313; IV. 0·8460; V. 0·864.

49. *Behaviour of Metallic Mercury at the Ordinary Temperature, and on Boiling with Water* (*to* § 84, *a*).

The following experiments were made in order to ascertain in what manner loss of metallic mercury occurs on drying, and also when it is boiled with water; and further, to determine the best method of drying.

6·4418 grams of perfectly pure mercury was treated in a watch-glass with distilled water, the water removed again as far as practicable by decantation, and finally by means of blotting paper; it weighed 6·4412 grams. After the mercury had been exposed for some hours to the air it weighed 6·4411 grams. The 6·4411 grams of mercury was placed under a bell-jar over sulphuric acid, the temperature being about 17°; and after 24 hours the weight had not altered in the least. The 6·4411 grams of mercury was then placed in a flask, plenty of distilled water added, and the whole boiled for 15 minutes violently. The mercury was then placed again upon the watch-glass, dried most carefully with blotting paper, and weighed; the weight was now 6·4402 grams. Finding that a trace of mercury had adhered to the paper, the same experiment was repeated with the 6·4402 grams. After 15 minutes' boiling with water, the mercury had again lost 0·0004 gram. The remaining 6·4398 grams, on being exposed to the air for 6 days in summer during very hot weather, lost only 0·0005 gram.

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* Journ. für prakt. Chem, 31, 385.

50. *Behaviour of Oxide of Copper on Ignition* (*to* § 85, *b*).

Pure oxide of copper, prepared from nitrate of copper, was ignited in a platinum crucible, then cooled over sulphuric acid, and weighed ; the weight was 3·542 grams. The oxide was next most intensely ignited for 5 minutes, over a BERZELIUS' lamp, and weighed as before, when the weight was not altered, and on again igniting the oxide for 5 minutes there was no change.

51. *Behaviour of Oxide of Copper in the Air* (*to* § 85, *b*).

A platinum crucible containing 4·3921 grams of gently ignited oxide of copper, prepared from the nitrate, was left for 10 minutes, covered with the lid, in a warm room, in winter ; the weight of the oxide of copper was found to have increased to 4·3939 grams.

The oxide of copper was then intensely ignited over a spirit-lamp ; after 10 minutes in the covered crucible, the weight had not perceptibly increased, and after 24 hours it had increased by 0·0036 gram.

52. *Behaviour of Sulphide of Bismuth on drying at* 100° (*to* § 86, *g*).

0·4558 gram of sulphide of bismuth, prepared in the wet way, was left in the desiccator on a watch glass, at the ordinary temperature ; after 3 hours, the weight was 0·4270, after 6 hours 0·4258, after 2 days the same.

0·3602 gram of the sulphide of bismuth dried in this way, after being heated for 15 minutes at 100°, weighed 0·3596, half an hour afterwards 0·3599, in half an hour more 0·3603, in two hours 0·3626. In a second experiment, the drying lasted 4 days, and a continual increase of weight was observed.

0·5081 gram of sulphide of bismuth dried in the desiccator was heated, in a boat, in a stream of carbonic acid ; after gentle ignition, the weight was 0·5002, and after repeated heating 0·4992. The sulphide of bismuth was visibly volatilized on ignition in a current of carbonic acid.

53. *Behaviour of Sulphide of Cadmium towards Ammonia, etc.* (*to* § 87, *c*).

Recently precipitated, pure sulphide of cadmium was diffused through water, and the following experiments were made with the mixture.

a. A portion was digested cold with ammonia in excess, and filtered. The filtrate remained perfectly clear on the addition of hydrochloric acid.

b. Another portion was digested hot with excess of ammonia, and filtered. This solution also remained perfectly clear on adding hydrochloric acid.

c. Another portion was digested for some time with solution of cyanide of potassium, and filtered. This filtrate also remained perfectly clear on adding hydrochloric acid.

d. Another portion was digested with hydrosulphide of sulphide of ammonium, and filtered. The turbidity produced on adding hydrochloric acid to this filtrate was pure white.

(A remark made by WACKENRODER, in BUCHNER'S Repertor. d. Pharm., 46, 226, induced the author to make these experiments.)

54. *Behaviour of Precipitated Sulphide of Antimony on drying* (*to* § 90, *a*).

0·2899 gram of pure precipitated sulphide of antimony which had been dried in the desiccator lost 0·0007 when dried at 100°.

0·4457 gram of the substance which had been dried at 100° lost 0·0011 water when heated to blackening in a stream of carbonic acid.

0·1932 gram of the substance dried at 100° gave up 0·0012 when heated to blackening in a stream of carbonic acid, and after stronger heating, during which fumes of sulphide of antimony began to escape, the total loss amounted to 0·0022 gram.

0·1670 gram of the substance, dried at 100°, lost 0·0005 gram on being heated to blackening in a stream of carbonic acid.

55. *Estimation of Ammonia, as in* § 99, 3.

The accuracy of this method of estimating ammonia is now so well established that any observations on the subject are rendered unnecessary.

56. *Estimation of Baryta by Precipitation with Carbonate of Ammonia* (*to* § 101, 2, *a*).

0·7553 gram of pure, ignited chloride of barium precipitated as in § 101, 2, *a*, gave 0·7142 BaO,CO_2, which corresponds with 0·554719 BaO = 73·44 per cent. (100 parts of BaCl should give 73·59 parts). The result, therefore, was 99·79 instead of 100.

57. *Estimation of Baryta in Organic Salts* (*to* § 101, 2, *b*).

0·686 gram of racemate of baryta ($2\ BaO,C_8H_4O_{10}+5$ aq.) treated according to § 101, 2, *b*, gave 0·408 of carbonate of baryta = 0·3169 BaO = 46·20 per cent. (calculated 46·38 per cent.) ; that is, 99·61 instead of 100.

58. *Estimation of Strontia as Sulphate of Strontia* (*to* § 102, 1, *a*).

a. An aqueous solution of 1·2398 grams of SrCl precipitated by sulphuric acid in excess, and the precipate washed with water, gave 1·4113 SrO,SO_3, which corresponds with 0·795408 SrO = 64·15 per cent. (calculated 65·38 per cent.) ; that is, 98·12 instead of 100.

b. 1·1510 grams of SrO,CO_2 dissolved in excess of hydrochloric acid, diluted, and precipitated with sulphuric acid, and the precipitate washed with water, gave 1·4024 SrO,SO_3 = 0·79039 SrO = 68·68 per cent. (calculated 70·07 per cent.) ; that is, 98·02 instead of 100.

59. *Estimation of Strontia as Sulphate, with Correction* (*to* § 102, 1, *a*).

The *filtrate* obtained in No. 58, *b*, weighed 190·84 grams. According to experiment No. 22, 11862 parts of water containing sulphuric acid dissolve 1 part of sulphate of strontia, therefore, 190·84 grams dissolve 0·0161 gram. The *washings* weighed 63·61 grams. According to experiment No. 21, 6895 parts of water dissolve 1 part of SrO,SO_3 ; therefore, 63·61 grams dissolve 0·0092 gram.

Adding 0·0161 and 0·0092 to the 1·4024 actually obtained, we find the total amount = 1·4277 grams, which corresponds with 0·80465 SrO = 69·91 per cent. in SrO,CO_2 (calculated 70·07 per cent.) ; that is, 99·77 instead of 100.

60. *Estimation of Strontia as Carbonate of Strontia* (*to* § 102, 2).

1·3104 grams of chloride of strontium, precipitated according to § 102, 2, gave 1·2204 SrO,CO_2, containing 0·8551831 SrO = 65·26 per cent. (calculated 65·38) ; that is, 99·82 instead of 100.

61. *Estimation of Lime as Sulphate of Lime by Precipitation* (*to* § 103, 1, *a*).

(In the experiments Nos. 61 to 64, pure air-dried carbonate of lime was used, in a portion of which the amount of anhydrous carbonate had been determined by very cautious heating. 0·7647 gram left 0·7581 gram, which weight remained unaltered on further, extremely gentle ignition ; "*air-dried carbonate*" contained accordingly 55·516 per cent. of lime.)

1·186 grams of "the air-dried carbonate of lime," dissolved in hydrochloric acid, and precipitated with sulphuric acid and alcohol, as in § 103, 1, *a*, gave 1·5949 grams of CaO,SO_3, containing 0·65598 CaO, that is, 55·31 per cent. (calculated 55·51), which gives 99·64 instead of 100.

62. *Estimation of CaO as CaO,CO_2, by Precipitation with Carbonate of Ammonia, and washing with Pure Water* (*to* § 103, 2, *a*).

A hydrochloric acid solution of 1·1437 grams of "the air-dried carbonate of lime" mentioned in No. 61, when dissolved in hydrochloric acid and precipitated as directed, gave 1·1243 grams of anhydrous carbonate of lime, corresponding with 0·629608 CaO = 55·05 per cent. (calculated 55·51 per cent.) which gives 99·17 instead of 100.

63. *Estimation of CaO as CaO,CO_2, by Precipitation with Oxalate of Ammonia from an Alkaline Solution* (*to* § 103, 2, *b*, *α*).

1·1734 grams of "the air-dried carbonate of lime" dissolved in hydrochloric acid, and treated as directed § 103, 2, *b*, *α*, gave 1·1632 grams CaO,CO_2 (reaction not alkaline), containing 0·651392 of CaO = 55·513 per cent. (calculated 55·516 per cent.), which gives 99·99 instead of 100.

64. *Estimation of Lime as Carbonate by Precipitation as Oxalate from an Acid Solution* (*to* § 103, 2, *b*, *β*).

0·857 gram of "the air-dried carbonate of lime," No. 61, dissolved in hydrochloric acid, and precipitated as in § 103, 2, *b*, *β*, gave 0·8476 CaO,CO_2 (which had no alkaline reaction, and was not in the slightest degree altered in weight by evaporation with carbonate of ammonia) containing 0·474656 CaO = 55·39 per cent. (calculated 55·51), which gives 99·78 instead of 100.

65. *Volumetric Estimation of Lime Precipitated as Oxalate* (*to* § 103, 3, *a and b*).

In one and the same solution of pure chloride of calcium, the lime was determined twice gravimetrically (by precipitation with oxalate of ammonia, and weighing as CaO,CO_2), twice by the alkalimetric method as in § 103, 3, *a*, and twice by precipitation with oxalate of ammonia and estimation of the oxalic acid in the precipitate by solution of permanganate of potassa. The following were the results obtained :

a. Gravimetrically.	*b*. Alkalimetrically.	*c*. By solution of permanganate of potassa.
0·5617 CaO,CO_2	0·5614	0·5613
0·5620 ,,	0·5620	0·5620

66. *Precipitation of Acetate of Zinc by Sulphuretted Hydrogen* (*to* § 108, *b*).

a. A solution of pure acetate of zinc was treated with the gas in excess, and allowed to remain for some time. The filtrate on being mixed with ammonia remained perfectly clear at first, and even after long standing deposited only a few scarcely visible flocks.

b. A solution of acetate of zinc to which a tolerably large amount of acetic acid had been added previously to the precipitation with sulphuretted hydrogen, showed exactly the same behaviour.

67. *Estimation of Iron as Sulphide* (*to* § 113, 2).

10 c.c. of a pure solution of ferric chloride, on precipitation with ammonia, gave 0·1453 Fe_2O_3 = 0·10171 Fe.

10 c.c. precipitated with ammonia and sulphide of ammonium, and treated after § 113, 2, yielded 0·1596 FeS = 0·10157 Fe.

10 c.c. again yielded 0·1605 FeS = 0·1021 Fe.

68. *Estimation of Lead as Chromate* (*to* § 116, 4).

The amount of lead in 1·0083 grams of pure nitrate of lead was estimated as chromate as in § 116, 4. The precipitate collected on a weighed filter, and dried at 100°, weighed 0·9871 gram=0·67833 PbO, or 67·3 per cent. Calculation gives 67·4.

0·9814 nitrate of lead again yielded 0·9625 gram of the chromate=67·4 per cent.

69. *Estimation of Copper by Precipitation with Zinc in a Platinum Basin* (*to* § 119, 2, *a*).

30·8820 grams of pure sulphate of copper was dissolved in water and made up to 250 c.c. ; 10 c.c. of the solution contained, therefore, 0·31387 gram of metallic copper.

a. 10 c.c. precipitated with zinc in a platinum dish, gave 0·3140=100·06 per cent.

b. In a second experiment, 10 c.c. gave 0·3138=100 per cent.

70. *Behaviour of Copper Precipitated by Zinc, when Ignited in Hydrogen* (*Vol. I. p.* 257, *foot-note*).

A dilute solution of sulphate of copper, acidified with hydrochloric acid, was precipitated with zinc in a platinum crucible, and the precipitate washed with water, then with alcohol, and dried at 100° ; 0·7961 gram of this was ignited for a quarter of an hour in a stream of hydrogen. It then weighed 0·7952 gram.

71. *Estimation of Copper as Cuprous Sulphocyanate* (*to* § 119, 3, *b*).

0·5965 gram of pure sulphate of copper was dissolved in a little water, and, after the addition of an excess of sulphurous acid, precipitated with sulphocyanate of potassium. The well-washed precipitate, when dried at 100°, weighed 0·2893, corresponding with 0·1892 CuO=31·72 per cent. As sulphate of copper contains 31·83 per cent., this gives 99·66 instead of 100.

72. *Estimation of Copper by De Haen's Method* (*to* § 119, 4, *a*).

Four 10 c.c.s of a solution of sulphate of copper, each 10 c.c. containing 0·0254 gram of metallic copper, were severally mixed with iodide of potassium, and then with 50 c.c. of a solution of sulphurous acid (50 c.c. corresponding with 12·94 c.c. of iodine solution). After addition of starch paste, iodine solution was added until the liquid became blue.

This required,

In *a*, 4·09 ; *b*, 3·95 ; *c*, 4·06 ; *d*, 3·95.

As 100 c.c. of iodine solution contained 0·58043 gram of iodine, this gives, instead of 0·0254 of copper.

For *a*, 0·0256 ; *b*, 0·0260 ; *c*, 0·0257 ; *d*, 0·0260.

Another experiment, made with 100 c.c. of the same solution of sulphate of copper, gave 0·2606 instead of 0·254 of copper. Nitrate of ammonia having been added to 10 c.c. of the solution of sulphate of copper, and then some dilute hydrochloric acid, 3·4 and 3·5 c.c. of iodine solution were required instead of 4 c.c., so that considerably more iodine had separated than corresponded with the oxide of copper.

73. *Action of Solution of Cyanide of Potassium on Ammoniacal Solution of Oxide of Copper* (*to* § 119, 4, *b*).

a. Each of three 10 c.c. solutions of sulphate of copper, containing 0·1 gram of sulphate of copper, was mixed with increasing quantities of solution of ammonia, and sufficient water to equalize the degree of concentration in the three portions; solution of cyanide of potassium was then added, drop by drop, until the blue colour had disappeared. This required the following quantities:

Solution of sulphate of copper.	Solution of ammonia.	Water.	Solution of cyanide of potassium.
10 c.c.	4 c.c.	12 c c.	6·7
10 c.c.	8 c.c.	8 c.c.	6·85
10 c.c.	16 c.c.	0 c.c.	7·1

Neutral salts of ammonia also exercise some influence, as the following experiments show, which were made the next day with the same solutions:

Sol. CuO,SO_3.	Sol. NH_3.	Water, &c.	Sol. KCy.
10 c.c.	2 c.c.	14 c.c.	6·70
10 c.c.	2 c.c.	14 c.c. sol. NH_4Cl (1 : 10)	7·40
10 c.c.	6 c.c.	10 c.c. water, 4 c.c. SO_3dil. (1 : 5	7·00
10 c.c.	2 c.c.	8 c.c. NH_4O,NO_5 (1 : 10) 6 c.c. water	7·30

b. Each of several 10 c.c. of a solution of sulphate of copper, containing 0·1 gram of the salt, was mixed with 10 c.c. of a solution of sesquicarbonate of ammonia (1 : 10), and after the addition of water or of solution of neutral ammonia salts, cyanide of potassium solution was added at a temperature of 60° until the blue colour had vanished.

c.c. CuO,SO_3.	c.c. $2NH_4O,3CO_2$.	Water, &c.	c.c. KCy.
10	10	10. water	i. 16·4 ii. 16·6
10	10	10. NH_4O,SO_3 (1 : 10)	i. 16·9 ii. 17·1
10	10	10. NH_4O,NO_5 (1 : 10)	i. 17·0 ii. 17·1
10	10	10. NH_4Cl (1 : 10)	i. 17·1 ii. 17·1

The addition of 2 drops of ferrocyanide of potassium (1 : 20) does not much assist in ascertaining the end re-action, as the solution, which towards the end is coloured red, gradually becomes pale yellow when more cyanide is added, and is not fully decolorized until more cyanide has been added, and the mixture has stood for some time.

74. *Precipitation of Nitrate of Bismuth by Carbonate of Ammonia* (*to* § 120, 1, *a*).

If a solution of nitrate of bismuth, no matter whether containing much or little free nitric acid, is mixed with water, precipitated with carbonate of ammonia and ammonia, and filtered without warming, the filtrate, on adding sulphuretted hydrogen water, becomes blackish-brown; if, however, the turbid mixture is heated for a short time nearly to boiling before filtering, sulphuretted hydrogen no longer colours the filtrate, or, at all events, the change of colour is hardly visible to the eye looking through the full test-tube from the top.

75. *Estimation of Antimony as Sulphide* (*to* § 125, 1).

0·559 gram of pure air-dried tartar emetic, treated according to § 125, 1, gave 0·2902 gram of tersulphide of antimony dried at 100°, =0·2492 gram, or 44·58 per cent. of teroxide of antimony. Heated to blackening in a current of carbonic acid, the precipitate lost 0·0079 gram (reckoned from a part to the whole), leaving accordingly 0·2823 gram of anhydrous tersulphide of antimony, which corresponds with 0·24245 gram, or 43·37 per cent. of teroxide of antimony. As the tartar emetic contains 43·70 per cent. of teroxide of antimony, the process gives, if the precipitate is dried at 100°, 102·01, and if heated to blackening, 99·24 instead of 100.

76. *Volumetric Estimation of Antimony* (*to* § 125, 3, *a*).

5·0822 grams of chemically pure tartar emetic were dissolved and made up to 250 c.c.

Four portions of this solution, of 10 c.c. each, were mixed, severally, with different quantities of a cold saturated solution of pure bicarbonate of soda, and with different quantities of water; after the addition of 2 c.c. of starch paste to each portion, solution of iodine (100 c.c. = 0·53064 of iodine, corresponding with 0·30501 of teroxide of antimony) was dropped in until the iodide of starch reaction made its appearance.

1. 10 c.c. of the tartar emetic solution + 5 c.c. of solution of $NaO,2CO_2$, required 29·9 c.c. of the iodine solution to impart to the liquid a reddish colour, which did not instantly disappear upon shaking; and 30·1 c.c. to produce a distinct blue tint; after some time, the latter also disappeared.

2. 10 c.c. of the tartar emetic solution + 10 c.c. of solution of $NaO,2CO_2$. After the addition of 29·2 c.c. of the iodine solution, the liquid just began to exhibit a red tint, which immediately disappeared; 29·4 c.c. produced a distinct blue coloration, which disappeared only after 15 minutes.

3. 10 c.c. of the tartar emetic solution + 20 c.c. of solution of $NaO,2CO_2$. After the addition of 29·2 c.c. of the iodine solution, the liquid just began to exhibit a red tint; 29·5 c.c. produced a distinct blue tint, which disappeared only after 15 minutes.

4. 10 c.c. of tartar emetic solution + 20 c.c. of solution of $NaO,2CO_2$ + 100 c.c. of water. With 29·2 c.c., first reddish coloration, with 29·5 distinctly blue.

The results of the three last experiments, therefore, agreed very well, and as 29·5 c.c. of iodine solution corresponds with 0·08998 of teroxide of antimony, which are contained in 0·20329 of tartrate of antimony and potassa, the two last experiments give 44·26 per cent. of teroxide of antimony in tartar emetic; the formula requires 43·70. If the first reddening of the liquid, which remains visible for a short time after stirring, is considered as the final reaction, only 29·2 c.c. of the iodine solution was required, which gives 43·81 of teroxide of antimony in tartar emetic.

77. *Action of Iodine Solution on Solution of Carbonate of Soda* (*to* § 125, 3, *a*).

A solution of pure monocarbonate of soda, perfectly free from reducing substances,* and containing 5 grams of anhydrous salt in 100 c.c., was used; the iodine solution contained 0·53064 gram of iodine in 100 c.c., and the temperature was 19·5°. The quantity of thin starch paste added in each experiment was 2 c.c. Two stages of the reaction were distinguished.

a. The point at which the liquid exhibited the first faint blue tint.

b. The point at which the liquid presented the same blue colour as a mixture of 30 c.c. of water with 2 c.c. of starch paste, and 1 drop of iodine solution.

	c.c. NaO,CO.	c.c. Water.	c.c. Iodine.	
			a.	*b.*
1.	20	0	0·2	0·4
2.	20	60	0·55	0·8
3.	20	120	0·8	1·2
4.	20	280	1·7	2·2

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* This is best prepared from thoroughly washed bicarbonate of soda; a drop of a dilute solution of permanganate of potassa imparted to 20 c.c. of it a red tint, which did not disappear on adding dilute sulphuric acid in excess.

Deducting in 1, 1 drop, in 2, 2 drops, in 3, 0·1 c.c., in 4, 0·2 c.c., of iodine solution, these being the quantities severally required to impart a blue tint to the pure water mixed with starch paste, the results of this series of experiments clearly show that the same quantity of carbonate of soda will prevent a larger amount of iodine from forming iodide of starch, the more considerable the volume of water present.

78. *Action of Iodine Solution on Solution of Bicarbonate of Soda* (*to* § 125, 3, *a*).

The experiments were made with a cold saturated solution of bicarbonate of soda, free from the monocarbonate, and from reducing substances; the other conditions were the same as in No. 77.

	c.c. $NaO,2CO_2$.	c.c. Water.	Iodine.	
			a	*b*
1.	20	0		1 drop.
2.	20	60	1 drop	0·05 c.c.
3.	20	120	0·05 c.c.	0·10 c.c.
4.	20	280	0·10 c.c.	0·25 c.c.

The results of this series of experiments clearly show that bicarbonate of soda exercises no influence on the iodide of starch reaction.

79. *Estimation of Arsenious Acid by Solution of Iodine* (*to* § 127, 5, *a*, 1).

2·5 grams of pure arsenious acid was dissolved in a solution of pure carbonate of soda, hydrochloric acid added to the dilute solution in very slight excess, and the whole made up to 250 c.c.; the temperature was 20°, and the iodine solution contained 0·53064 gram of iodine in 100 c.c.

1. 10 c.c. of this solution + 20 c.c. of a solution of bicarbonate of soda saturated at 20°, + 2 c.c. starch paste, required 49·05 c.c. of the iodine solution to impart a reddish tint to the liquid, which after a short time disappeared; and 49·25 c.c. to produce a distinct blue coloration.

2. Same conditions as in 1, but with addition of 250 c.c. of water; first appearance of a light bluish tint at 49·1 c.c., and a distinct blue at 49·25 c.c. of the iodine solution.

3. Same conditions as in 1, but substituting for the 20 c.c. of solution of bicarbonate of soda, 10 c.c. of a solution of perfectly pure carbonate of soda (1 : 20), prepared from thoroughly washed bicarbonate. First reddish tint at 49·25 c.c., and a distinct blue coloration at 49·32 c.c. of iodine solution.

4. Same conditions as in 3, with 20 c.c. of solution of carbonate of soda instead of 10 c.c. Distinct blue colour at 49·27 c.c.

5. Same as in 4, + 250 c.c. of water. Distinct blue colour at 49·3 c.c.

6. Same as in 5, but with 50 c.c. of solution of carbonate of soda instead of 20 c.c. Distinct blue colour with 49·46 c.c. of the iodine solution.

These results agree well together. 49 c.c. of iodine solution was clearly sufficient to convert the arsenious into arsenic acid, corresponding with 0·1014 gram of arsenious acid, whilst the 10 c.c. of solution used contained 0·100 gram.

80 *Estimation of Phosphoric Acid as Pyrophosphate of Magnesia* (*to* § 134, *b*, *a*).

1·9159 and 2·0860 grams of pure crystallized phosphate of soda, treated as directed in § 134, *b*, *a*, gave 0·5941 and 0·6494 gram of pyrophosphate of magnesia, respectively. These give 19·83 and 19·91 per cent. of phosphoric acid in phosphate of soda, instead of 19·83 per cent.

81. *Estimation of Phosphoric Acid as Phosphate of Uranium* (*to* § 134, *c*).

30 c.c. of a solution of pure phosphate of soda, treated with sulphate of magnesia, chloride of ammonium, and ammonia, as directed in § 134, *b*, *a*, gave 0·3269 gram of pyrophosphate of magnesia. 10 c.c. contained accordingly 0·06982 gram of phosphoric acid.

10 c.c. of the same solution was then precipitated with acetate of uranium as directed § 134, *c*. The ignited precipitate was treated with a little nitric acid, and again ignited, when it weighed 0·3478 gram, corresponding with 0·06954 gram of phosphoric acid.

82. *Estimation of Free Sulphuretted Hydrogen by Means of Solution of Iodine* (*to* § 148, I., *a*).

The experiments were made to settle the following questions :

a. Does the quantity of iodine required remain the same for different degrees of dilution ?

b. Does the equation $HS + I = HI + S$ really represent the decomposition which takes place ?

The sulphuretted hydrogen water used was contained in a flask closed by a doubly-perforated cork ; into one aperture a siphon with pinchcock was fitted, to draw off the solution ; into the other aperture a short open tube, which did not dip into the liquid.

Question a.

α. About 30 c.c. of iodine solution was introduced into a flask, which was then tared, and sulphuretted hydrogen water added until the yellow colour had just disappeared ; it was then closed, weighed, starch paste added, and then solution of iodine until the liquid became blue.

70·2 grams of HS water required 23·4 c.c. of iodine solution, 100 accordingly 33·33 c.c.

68·4 grams required 22·7 c.c. of iodine solution, 100 accordingly 33·20 c.c.

β. Same process ; but the solution was diluted with water free from air.

61·5 grams of HS water + 200 grams of water required 20·7 c.c. of iodine solution, 100 accordingly 33·65 c.c.

54·4 grams + 400 grams of water required 17·7 c.c. of iodine solution, 100 accordingly 33·77.

The iodine solution contained 0·00498 iodine in 1 c.c. Considering that the addition of a larger volume of water necessarily involves a slight increase in the quantity of iodine solution, these results may be considered as agreeing sufficiently well.

Question b.

According to *a*, 100 grams of the HS water contained 0·02215 gram of HS, assuming the proportion to be 100 : 33·2.

173·6 grams of the same HS water were, immediately after the experiments in *a*, drawn off into a hydrochloric acid solution of arsenious acid ; after 24 hours, the tersulphide of arsenic was collected, dried at 100°, and weighed. 0·0920 gram was obtained, corresponding with 0·03814 HS, or 0·02197 per cent.

The second question, therefore, also is answered in the affirmative.

83. *Solution of Chloride of Magnesium dissolves Oxalate of Lime* (*to* § 154, 6).

If some chloride of calcium is added to a solution of chloride of magnesium, and then a little oxalate of ammonia, no precipitate is formed ; but on slightly increasing the quantity of oxalate of ammonia, a trifling precipitate gradually separates after some time.

If an excess of oxalate of ammonia is added, the whole of the lime is thrown down, but the precipitate contains oxalate of magnesia. This shows that to effect the separation of the two bases by oxalate of ammonia, excess of the reagent must be added, but if much magnesia is present, the operator must expect to throw down some of the magnesia along with the lime, as the following experiments (No. 84) clearly show.

84. *As to the Separation of Lime from Magnesia* (*to* § 154, 6).

The solutions employed in the following experiments were, a solution of chloride of calcium, 10 c.c. of which corresponded with 0·5618 CaO,CO_2; a solution of chloride of magnesium, containing 0·250 MgO in 10 c.c.; a solution of chloride of ammonium (1 : 8); solution of ammonia, containing 10 per cent. NH_3; a solution of 1 part of oxalate of ammonia in 24 of water; acetic acid, containing 30 per cent. AcHO.

The precipitation was effected at the ordinary temperature, the precipitate of oxalate of lime being filtered off after 20 hours.

a. Influence of the degree of dilution.

α. 10 c.c. MgCl, 10 c.c. CaCl, 10 c.c. NH_4Cl, 4 drops NH_4O, 50 c.c. water, 20 c.c, $NH_4O,\bar{O}$. Result, 0·5705 gram of CaO,CO_2.

β. Same as α, with 150 c.c. water instead of 50 c.c. Result, 0·5670 CaO,CO_2.

b. Influence of excess of ammonia.

Same as *a*, β + 10 c.c. NH_4O. Result, 0·5614 gram of CaO,CO_2.

c. Influence of excess of chloride of ammonium.

Same as *a*, β + 40 c.c. NH_4Cl. Result, 0·5652 gram.

d. Influence of excess of ammonia and chloride of ammonium.

Same as *a*, β + 30 c.c. NH_4Cl + 10 c.c. NH_4O. Result, 0·5613 gram.

e. Influence of free acetic acid.

Same as *a*, β, only with 6 drops $\bar{A}$, and 4 drops NH_4O. Result, 0·5594 gram.

f. Influence of excess of oxalate of ammonia, in feebly alkaline solution.

Same as *a*, β + 20 c.c. $NH_4O,\bar{O}$. Result, 0·5644 gram of CaO,CO_2.

g. Influence of excess of oxalate of ammonia, in strongly alkaline solution.

Same as *a*, β, + 10 c.c. NH_4O + 20 c.c. $NH_4O,\bar{O}$. Result, 0·5644 gram.

h. Influence of excess of oxalate of ammonia, in presence of much NH_4Cl *and* NH_4O.

Same as *a*, β, + 10 NH_4O + 30 NH_4Cl + 20 $NH_4O,\bar{O}$. Result, 0·5709 gram.

i. Influence of excess of oxalate of ammonia, in solution slightly acidified with acetic acid.

Same as *a*, β,–4 drops NH_4O + 6 drops $\bar{A}$ + 20 c.c. $NH_4O,\bar{O}$. Result, 0·5661 gram.

Consequently, when a notable amount of magnesia is present, there is always a chance of oxalate of magnesia, or oxalate of magnesia and ammonia being precipitated along with the oxalate of lime.

Another series of experiments in which a solution of oxalate of magnesia in hydrochloric acid was mixed with ammonia under varying circumstances, proved also that, in presence of a notable quantity of magnesia, oxalate of magnesia, or oxalate of magnesia and ammonia, will always separate after some time, no matter whether in a cold or a warm place.

In a third series of experiments, the separation of lime from magnesia was effected by double precipitation, exactly as in § 154 (**36**). The same solutions were employed as in the first series, with the exception of the chloride of magnesium, which contained 0·2182 gram of MgO, in 10 c.c.

10 c.c. CaCl, 30 c.c. MgCl, 20 c.c. NH_4Cl, 300 c.c. water, 6 drops ammonia and a sufficient excess of oxalate of ammonia. Results, in two experiments

0·5621 and 0·5652, mean 0·5636, instead of 0·5618, CaO,CO_2 ; also 0·6660 and 0·6489 MgO, mean 0·6574, instead of 0·6546.

85. *Sensibility of various Metallic Solutions towards Sulphuretted Hydrogen* (*to* § 208, 8 ; *this vol. p.* 142).

Five portions, of 500 c.c. each, were taken, of a highly dilute aqueous solution of sulphuretted hydrogen, containing 0·003 HS in 1000 parts.

There was added—

a, CuCl, gave a blackish coloration.

b, AsO_3 dissolved in hydrochloric acid gave a precipitate only after 12 hours ; the liquid had not quite cleared then.

c, CdCl, gave a beautiful flocculent precipitate after 1 hour.

d, AgO,NO_5. The solution appeared blackish ; it required 12 hours for the precipitate to subside completely.

e, HgCy. The solution appeared blackish ; it required 12 hours for the precipitate to subside.

86. *Estimation of Sulphuretted Hydrogen by Solution of Cadmium* (*to* § 208, 8).

230·3 grams of the same sulphuretted hydrogen water which had served for the experiments in No. 82, and containing in 100 grams 0·02215 of HS, was mixed with solution of cadmium in excess, filtered after 24 hours, and the precipitate washed, dried at 100°, and weighed. Result, 0·2395. If the precipitate had consisted of pure sulphide of cadmium, it would have given, by calculation, 0·0247 per cent. HS, consequently too much. A portion of it was therefore deflagrated with carbonate of soda and nitrate of potassa and the residue tested for chlorine ; a distinct reaction was observed.

87. *Estimation of Carbonic Acid in Seltzer Water* (*to* § 209, 5, *this vol. p.* 156).

The total carbonic acid in the mineral water of Niederselters was determined exactly as described in this vol. p. 156, 5. The following were the results :

1. *Water from the top of the shaft* (collected with a plunging siphon and transferred to bottles provided with hydrate of lime and chloride of calcium).
   221·331 water yielded 0·7640 CO_2, = 3·45184 per thousand.
   221·246 ,, ,, 0·7654 ,, = 3·45949 ,,
2. *Water from the bottom of the shaft* (collected with the apparatus Fig. 78, p. 140 of this vol.).
   250·398 water yielded 0·8654 CO_2, = 3·45609 per thousand.
   230·044 ,, ,, 0·7952 ,, = 3·45673 ,,

88. *Chlorimetrical Experiments* (*to* § 233, *et seq*).

10 grams of chloride of lime were rubbed up with water, made up to one litre, and the following experiments made :

a. By PENOT's method (§ 233, this vol. p. 243) ; obtained 23·5 and 23·5 per cent.

b. By means of iron (modification 1, this vol. p. 246) ; obtained 23·6 per cent.

c. By BUNSEN's method (this vol. p. 245) ; results, 23·6, and 23·6 per cent.

89. *Drying of Black oxide of Manganese* (*to* § 246, I., *this vol. p.* 290.

Four small pans, containing each 8 grams of manganese peroxide of 53 per cent., were first heated in the water-bath. After 3 hours, I. had lost 0·145 ; after 6 hours, II. 0·15 ; after 9 hours, III. 0·15 ; after 12 hours, IV. 0·15 gram.

When I. and II. had been left, loosely covered, in the room for 12 hours, II. was found to weigh exactly as much as at first; I. wanted only 0·01 gram of the original weight.

The four pans were now heated for two hours at 120°; after cooling, each had lost 0·180 of the original weight. After I. and II. had been left, loosely covered, in the room for 60 hours, they were both found to have again acquired their original weight by attracting moisture. III. and IV. were heated for 2 hours at 150°; the loss of weight in both cases was 0·215 gram. Having been left, loosely covered, in the room for 72 hours, both were found to weigh 0·05 less than at first. Assuming the hygroscopic moisture expelled to be re-absorbed by exposure to the air, this shows that at 150° a little chemically combined water escapes along with the moisture, and accordingly that the temperature at which the sample is dried should not exceed 120°.

The author's experiments are described in detail in DINGLER'S polyt. Journ., 135, 277 et seq.

90. *Behaviour of Hydrated Oxide of Nickel towards Boiling Water* (*to foot-note, this vol. p.* 301).

A solution of 2 grams of crystallized sulphate of nickel, to which 2 to 3 grams of chloride of potassium had been added, was poured into excess of dilute boiling solution of potash, and the precipitate of hydrated oxide of nickel washed with boiling distilled water, first by decantation and then on the filter, until the washings no longer gave any turbidity with nitrate of silver. The filtrate and washings were then removed, and the precipitate on the filter again washed with boiling distilled water until 1 litre had passed through. The filtrate was then evaporated to dryness, the residue treated with a very small quantity of hydrochloric acid, ammonia added in excess, and the whole filtered: the solution, which had only the slightest bluish tinge, was acidified with acetic acid and precipitated hot by sulphuretted hydrogen. A very small quantity of sulphide of nickel was thus obtained, which, when converted into anhydrous sulphate of nickel, weighed 0·0005 gram, corresponding with 0·00024 gram of oxide of nickel.

91. *Determination of Silver in Argentiferous Lead* (*to this vol. p.* 369).

a. 10 grams of sulphide of lead and 0·3 gram of sulphide of silver were treated as directed in p. 365, 3, *a*, α, and the silver in the button determined as in p. 369, 4, *a*. Obtained a button of 8·093, and from this, 0·3458 gram of chloride of silver, instead of 0·347 gram.

b. 5 grams of sulphide of lead and 0·05 gram of sulphide of silver gave a button of 4·025 gram and 0·0562 gram of chloride of silver, instead of 0·0578 gram.

c. 10 grams of sulphide of lead and 0·01 gram of sulphide of silver gave a button of 7·7384 gram and 0·0106 gram of chloride of silver instead of 0·0115 gram.

II.—TABLES FOR THE CALCULATION OF ANALYSES.

TABLE I.

EQUIVALENTS OF THE ELEMENTS CONSIDERED IN THE PRESENT WORK.*

Aluminium	Al	13·75	(Dumas)
Antimony	Sb	122·00	(Dumas)
Arsenic	As	75·00	(Pelouze, Berzelius)
Barium	Ba	68·50	(Dumas)
Bismuth	Bi	208·00	(Schneider)
Boron	B	11·00	(Berzelius)
Bromine	Br	79·95	(Stas)
Cadmium	Cd	56·00	(C. v. Hauer)
Cæsium	Cs	133·00	(Johnson and Allen, Bunsen)
Calcium	Ca	20·00	(Dumas, Erdmann and Marchand)
Carbon	C	6·00	(Dumas, Erdmann and Marchand)
Chlorine	Cl	35·46	(Marignac, Stas)
Chromium	Cr	26·24	(Berlin, Péligot)
Cobalt	Co	29·50	(Rothoff, Dumas)
Copper	Cu	31·70	(Erdmann and Marchand)
Fluorine	Fl	19·00	(Louyet)
Gold	Au	196·71	(Berzelius)
Hydrogen	H	1·00	(Dumas)
Iodine	I	126·85	(Stas)
Iron	Fe	28·00	(Erdmann and Marchand)
Lead	Pb	103·50	(Berzelius, Dumas)

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* The above Table contains the equivalents considered most trustworthy at the time the first volume of the sixth edition of this work was in preparation ; but as, in the interim, these figures have been recalculated and also new determinations carried out, a second Table (Table II.) is given in which the equivalents in Table I. are compared with those resulting from Clarke's calculations ("The Constants of Nature," Part V. Washington : Smithsonian Institution, 1880 ; Zeitschr. f. anal. Chem. 22, 302). As the figures in both sets are referred to Oxygen = 8 they are directly comparable one with another.

In order to demonstrate that Clarke's calculations yielded almost exactly the same results as those of Lothar Meyer and K. Seubert ("Die Atomgewichte der Elemente," 1883 ; Breitkopf and Hartel, Leipzig, Zeitschr. f. anal. Chem. 22, 639) a comparative Table (III.) of these is also given. In this, the figures express the atomic weights referred to hydrogen as unit and on the assumption that the relation of the hydrogen atom to that of oxygen is as 1 to 15·96 ; they are, therefore (if the atomic weights are calculated to the equivalents), not directly comparable with the figures in Tables I. and II. Finally, in Table IV. are given the equivalent weights based on determinations carried out subsequently to the publication of Clarke's numbers, and those of Meyer and Seubert.

Lithium	Li	7·02	(Stas)
Magnesium	Mg	12·00	(Marchand and Scheerer)
Manganese	Mn	27·50	(v. Hauer, Dumas)
Mercury	Hg	100·00	(Erdmann and Marchand)
Molybdenum	Mo	48·00	(Dumas, Debray)
Nickel	Ni	29·50	(Rothoff, Marignac, Dumas)
Nitrogen	N	14·04	(Stas)
Oxygen	O	8·00	
Palladium	Pd	53·29	(Berzelius)
Phosphorus	P	31·00	(Schrötter)
Platinum	Pt	98·59	(Berzelius)
Potassium	K	39·13	(Stas)
Rubidium	Rb	85·40	(Bunsen, Piccard)
Selenium	Se	39·5	(Berzelius, Sacc, Erdmann and Marchand—mean)
Silicon	Si	14·00	(Dumas)
Silver	Ag	107·93	(Stas)
Sodium	Na	23·04	(Stas)
Strontium	Sr	43·75	(Dumas)
Sulphur	S	16·00	(Erdmann and Marchand)
Thallium	Tl	203·64	(Crookes)
Tin	Sn	59·00	(Dumas)
Titanium	Ti	25·00	(Pierre)
Uranium	Ur	59·40	(Ebelmen)
Zinc	Zn	32·53	(Axel Erdmann)

TABLE II.

COMPARATIVE TABLE OF THE EQUIVALENT WEIGHTS OF THE ELEMENTS.

—	The Equivalents used in the foregoing Work O=8.	Equivalents according to CLARKE'S Calculations.* O=8.	—
Aluminium	13·75	13·537	
Antimony	122·00	120·231	According to COOKE, junr., and SCHNEIDER.
Arsenic	75·00	75·090	
Barium	68·50	68·503	
Beryllium	—	4·553	NILSON and PETTERSON (for Beryllia BeO).
Bismuth	208·00	208·001	SCHNEIDER.
Boron	11·00	10·966	
Bromine	79·95	79·951	
Cadmium	56·00	56·046	
Cæsium	133·00	132·918	
Calcium	20·00	20·041	
Carbon	6·00	6·0005	
Cerium	—	70·373	BÜHRIG makes C. =70·7615.
Chlorine	35·46	35·451	
Chromium	26·24	26·064	SIEWERT.
Cobalt	29·50	29·511	
Copper	31·70	31·659	
Didymium	—	72·453	CLEVE finds for $SO_3=40$, Di=73·51.
Erbium	—	83·136	Only according to CLEVE.
Fluorine	19·00	19·027	
Gallium	—	34·481	Incompletely determined.
Gold	196·71	196·606	
Hydrogen	1·00	1·0023	
Indium	—	56·829	
Iodine	126·85	126·848	
Iridium	—	96·547	SEUBERT.
Iron	28·00	28·021	
Lanthanium	—	69·422	
Lead	103·50	103·473	
Lithium	7·020	7·0235	

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* Zeitschr. f. anal. Chem. 22, 302.

TABLE II.—(*continued*.)

—	The Equivalents used in the foregoing Work. O=8.	Equivalents according to CLARKE'S Calculations.* O=8.	—
Magnesium .	12·00	12·007	MARCHAND and SCHEERER.
Manganese .	27·50	27·014	SCHNEIDER and RAWACK.
Mercury . .	100·00	100·085	
Molybdenum	48·00	47·873	
Nickel . .	29·50	29·031	SCHNEIDER, SOMMARUGA and LEE.
Niobium . .	—	94·027	One determination only.
Nitrogen . .	14·04	14·029	
Osmium . .	—	99·475	Very doubtful.
Oxygen . .	8·00	8·000	
Palladium .	53·29	52·990	Uncertain.
Phosphorus .	31·00	31·029	
Platinum. .	98·59	97·433	SEUBERT.
Potassium .	39·13	39·109	
Rhodium. .	—	52·142	Uncertain.
Rubidium .	85·40	85·529	
Ruthenium .	—	52·228	Uncertain.
Scandium .	—	22·040	
Selenium. .	39·50	39·489	
Silicon . .	14·00	14·130	Very uncertain.
Silver . . .	107·93	107·923	
Sodium . .	23·04	23·051	
Strontium .	43·75	43·787	
Sulphur . .	16·00	16·029	
Tantalum .	—	182·562	
Tellurium .	—	64·127	Incomplete determination.
Thallium. .	203·64	204·183	CROOKES.
Thorium . .	—	116·975	
Tin . . .	59·00	58·984	
Titanium. .	25·00	24·980	Incomplete determination.
Tungsten. .	—	92·016	
Uranium . .	59·40	59·757	
Vanadium .	—	25·686	
Ytterbium .	—	86·579	$SO_3=40$, showed Yb = 86·508.
Yttrium . .	—	45·011	Doubtful.
Zinc . . .	32·53	32·527	AXEL ERDMANN.
Zirconium .	—	44·786	Doubtful.

* Zeitschr. f. anal. Chem. 22, 302.

TABLE III.

ATOMIC WEIGHTS OF THE ELEMENTS (HYDROGEN=1, OXYGEN=15·96).

—	According to CLARKE.	According to L. MEYER and K. SEUBERT.
Aluminium	27·009	27·04
Antimony	119·955	119·6
Arsenic	74·918	74·9
Barium	136·763	136·86
Beryllium	9·085	9·08
Bismuth	207·523	207·5
Boron	10·941	10·9
Bromine	79·768	79·76
Cadmium	111·835	111·70
Cæsium	132·583	132·7
Calcium	39·990	39·91
Carbon	11·9736	11·97
Cerium	140·424	141·2
Chlorine	35·370	35·37
Chromium	52·009	52·45
Cobalt	58·887	58·6
Copper	63·173	63·18
Didymium	144·573	145·0
Erbium	165·891	166·0
Fluorine	18·984	19·06
Gallium	68·854	69·9
Gold	196·155	196·2
Hydrogen	1·000	1·00
Indium	113·398	113·4
Iodine	126·557	126·54
Iridium	192·651	192·5
Iron	55·913	55·88
Lanthanium	138·526	138·5
Lead	206·471	206·39
Lithium	7·0073	7·01
Magnesium	23·959	23·94
Manganese	53·906	54·8
Mercury	199·712	199·8
Molybdenum	95·527	95·9

TABLE III.—(*continued.*)

—	According to Clarke.	According to L. Meyer and K. Seubert.
Nickel	57·928	58·6
Niobium	93·812	93·7
Nitrogen	14·021	14·01
Osmium	198·494	195
Oxygen	15·9633	15·96
Palladium	105·737	106·2
Phosphorus	30·958	30·96
Platinum	194·415	194·3
Potassium	39·019	39·03
Rhodium	104·055	104·1
Rubidium	85·251	85·2
Ruthenium	104·217	103·5
Scandium	43·980	43·97
Selenium	78·797	78·87
Silicon	28·195	28·00
Silver	107·675	107·66
Sodium	22·998	22·995
Strontium	87·374	87·3
Sulphur	31·984	31·98
Tantalum	182·144	182·0
Tellurium	127·960	127·7*
Thallium	203·715	203·7
Thorium	233·414	231·96
Tin	117·698	117·35
Titanium	49·846	50·25
Tungsten	183·610	183·6
Uranium	238·482	239·8
Vanadium	51·256	51·1
Ytterbium	172·761	172·6
Yttrium	89·816	89·6
Zinc	64·9045	64·88
Zirconium	89·367	90·4

* Or Te = 126·3.

TABLE IV.

EQUIVALENTS OF THE MORE IMPORTANT ELEMENTS DETERMINED SINCE THE CALCULATIONS OF CLARKE, AND OF L. MEYER AND K. SEUBERT.

Element.	Equivalent Determined by	Reference.	O=8 Result of the new Determination.	O=8 The equivalence adopted in the present book.
Aluminium.	BAUBIGNY.	Compt. rend. 97, 1369 ; Zeitschr. f. anal. Chem. 23, 607.	13·508	13·75
Antimony.	BONGARTZ.	Ber. deutsch. chem. Gesell. 16, 1942 ; Zeitschr. f. anal. Chem. 23, 294.	120·470	122·00
,,	POPPER.	Ann. d. Chem. und Pharm. 233, 157.	121·303	122·00
Bismuth.	MARIGNAC.	Archiv. des. scienc. phys. et nat. [iii.] 10, 5 and 193 ; Zeitschr. f. anal. Chem. 23, 124.	208·160	208·00
Carbon.	VAN DER PLAATS.	Compt. rend. 100, 52 ; Zeitschr. f. anal. Chem. 24, 648.	6·0014	6·00
Cerium.	H. ROBINSON.	Chem. News, 50, 251 ; Zeitschr. f. anal. Chem. 25, 148.	70·129	
,,	B. BRAUNER.	Sitzungsber. der. k. Akademie d. Wissenschaft in Wien, II. Pt. 92, 814 ; Zeitschr. f. anal. Chem. 25, 611.	70·110	
Cobalt.	CL. ZIMMERMANN.	Ann. d. Chem. und Pharm. 232, 339.	29·445	29·50
Copper.	BAUBIGNY.	Compt. rend. 97, 854, 906 and 951 ; Zeitschr. f. anal. Chem. 23, 288.	31·698	31·70
Germanium.	CL. WINKLER.	Journ. f. prakt. Chem. (n.s.) 34, 203.	36·2506	
Lanthanium.	MARIGNAC.	Ann. Chim. phys. [iv.] 30, 67 ; Zeitschr. f. anal. Chem. 23, 140.	69·405*	
,,	CLEVE.	Bull. Soc. chim. de Paris, 39, 131 ; Zeitschr. f. anal. Chem. 23, 140.	69·110*	

* Oxide of lanthanium = L_2O_3.

Magnesium.	Marignac.	Archiv. des sciences phys. et nat. [iii.] 10, 5 and 193; Zeitschr. f. anal. Chem. 23, 139.	12·185	12·00
Manganese.	Dewar and Scott.	Chem. News, 47, 98; Zeitschr. f. anal. Chem. 22, 482.	27·519	27·50
”	Marignac.	Archiv. des sciences phys. et nat. [iii.] 10, 5 and 193; Zeitschr. f. anal. Chem. 23, 125.	27·500	27·50
Nickel.	Cl. Zimmermann.	Ann. d. Chem. u. Pharm. 232, 344.	29·3525	29·50
”	Baubigny.	Compt. rend. 97, 854, 906 and 951; Zeitschr. f. anal. Chem. 23, 292.	29·339	29·50
Nitrogen.	Stas.	*See* Potassium.	14·055	14·04
Phosphorus.	Van der Plaats.	Compt. rend. 100, 52: Zeitschr. f. anal. Chem. 24, 649.	30 975	31·00
Platinum.	Halberstadt.	Ber. deutsch. chem. Gesell. 17, 2962; Zeitschr. f. anal. Chem. 25, 296.	97·532	98·59
Potassium.	Stas.	Mémoires de l'académie royale des sciences, des lettres, et des beaux-arts de Belgique, 43, 1842: Zeitschr. f. anal. Chem. 25, 288.	39·1425	39·13
Silver.	Stas.	*See* Potassium.	107·930	107·93
Sodium.	Stas.	*See* Potassium.	23·0455	23·04
Tellurium.	Brauner.	Prot. i. J. d. russ. phys. chem. Gesellschaft, 1883 [i.], 433; Zeitschr. f. anal. Chem. 23, 612.	62·500	
Tin.	Van der Plaats.	Compt. rend. 100, 52; Zeitschr. f. anal. Chem. 24, 651.	59·038	59·00
Titanium.	Thorpe.	Chem. News, 48, 251; Zeitschr. f. anal. Chem. 23, 609.	24·06	25·00
Uranium.	Cl. Zimmermann.	Ann. d. Chem. u. Pharm. 232, 317.	59·874	59·40
Yttrium.	Cleve.	Compt. rend. 95, 1225; Zeitschr. f. anal. Chem. 22. 484.	44·510*	
Zinc.	Marignac.	*See* Bismuth.	32·665	32·53
”	Baubigny.	Compt. rend. 97, 854, 906 and 951; Zeitschr. f. anal. Chem. 23, 291.	32·667	32·53
”	Van der Plaats.	Compt. rend. 100, 52; Zeitschr. f. anal. Chem. 24, 651.	32·590	32·53

* Oxide of Yttrium = Y_2O_3.

TABLE V.

COMPOSITION OF THE BASES AND OXYGEN ACIDS.*

a. BASES.

GROUP I.			
Cæsia	Cs	133·00	94·33
	O	8·00	5·67
	CsO	141·00	100·00
Rubidia	Rb	85·40	91·43
	O	8·00	8·57
	RbO	93·40	100·00
Potassa	K	39·13	83·03
	O	8·00	16·97
	KO	47·13	100·00
Soda	Na	23·04	74·23
	O	8·00	25·77
	NaO	31·04	100·00
Lithia	Li	7·02	46·74
	O	8·00	53·26
	LiO	15·02	100·00
Oxide of Ammonium	NH_4	18·04	69·28
	O	8·00	30·72
	NH_4O	26·04	100·00
GROUP II.			
Baryta	Ba	68·50	89·54
	O	8·00	10·46
	BaO	76·50	100·00
Strontia	Sr	43·75	84·54
	O	8·00	15·46
	SrO	51·75	100·00
Lime	Ca	20·00	71·43
	O	8·00	28·57
	CaO	28·00	100·00

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* These Tables are founded on the equivalent weights given in the book. The oxygen compounds of those elements which have suffered any appreciable change in consequence of recalculation or of new determinations, are indicated by an asterisk (*)

Magnesia*	Mg	12·00	60·00
	O	8·00	40·00
	MgO	20·00	100·00
GROUP III.			
Alumina*	Al_2	27·50	53·40
	O_3	24·00	46·60
	Al_2O_3	51·50	100·00
Sesquioxide of Chromium*	Cr_2	52·48	68·62
	O_3	24·00	31·38
	Cr_2O_3	76·48	100·00
GROUP IV.			
Oxide of Zinc	Zn	32·53	80·26
	O	8·00	19·74
	ZnO	40·53	100·00
Manganous Oxide	Mn	27·50	77·46
	O	8·00	22·54
	MnO	35·50	100·00
Sesquioxide of Manganese	Mn_2	55·00	69·62
	O_3	24·00	30·38
	Mn_2O_3	79·00	100·00
Protoxide of Nickel*	Ni	29·50	78·67
	O	8·00	21·33
	NiO	37·50	100·00
Protoxide of Cobalt*	Co	29·50	78·67
	O	8·00	21·33
	CoO	37·50	100·00
Sesquioxide of Cobalt*	Co_2	59·00	71·08
	O_3	24·00	28·92
	Co_2O_3	83·00	100·00
Ferrous Oxide	Fe	28·00	77·78
	O	8·00	22·22
	FeO	36·00	100·00
Ferric Oxide	Fe_2	56·00	70·00
	O_3	24·00	30·00
	Fe_2O_3	80·00	100·00
GROUP V.			
Oxide of Silver	Ag	107·93	93·10
	O	8·00	6·90
	AgO	115·93	100·00

Oxide of Lead	Pb	103·50	92·83
	O	8·00	7·17
	PbO	111·50	100·00
Mercurous Oxide	Hg_2	200·00	96·15
	O	8·00	3·85
	Hg_2O	208·00	100·00
Mercuric Oxide	Hg	100·00	92·59
	O	8·00	7·41
	HgO	108·00	100·00
Suboxide of Copper	Cu_2	63·40	88 80
	O	8·00	11 20
	Cu_2O	71 40	100·00
Oxide of Copper	Cu	31·70	70·85
	O	8·00	20·15
	CuO	39·70	100 00
Oxide of Bismuth	Bi	208·00	89 66
	O_3	24 00	10·34
	BiO_3	232·00	100·00
Oxide of Cadmium	Cd	56·00	87·50
	O	8·00	12·50
	CdO	64·00	100·00
GROUP VI.			
Oxide of Gold	Au	196·71	89·13
	O_3	24·00	10·87
	AuO_3	220·71	100·00
Oxide of Platinum °	Pt	98·59	86·04
	O_2	16·00	13·96
	PtO_2	114·59	100·00
Oxide of Antimony °	Sb	122·00	83·56
	O_3	24·00	16·44
	SbO_3	146·00	100·00
Stannous Oxide	Sn	59·00	88·06
	O	8 00	11·94
	SnO	67·00	100·00
Stannic Oxide	Sn	59·00	78·67
	O_2	16·00	21·33
	SnO_2	75·00	100·00

Arsenious acid	As	75·00	75·76
	O_3	24·00	24·24
	AsO_3	99·00	100·00
Arsenic acid	As	75·00	65·22
	O_5	40·00	34·78
	AsO_5	115·00	100·00

b. ACIDS.

Chromic acid*	Cr	26·24	52·23
	O_3	24·00	47·77
	CrO_3	50·24	100·00
Sulphuric acid	S	16·00	40·00
	O_3	24·00	60·00
	SO_3	40·00	100·00
Phosphoric acid	P	31·00	43·66
	O_5	40·00	56·34
	PO_5	71·00	100·00
Boric acid	B	11·00	31·43
	O_3	24·00	68·57
	BO_3	35·00	100·00
Oxalic acid	C_4	24·00	33·33
	O_6	48·00	66·67
	C_4O_6	72·00	100·00
Carbonic acid	C	6·00	27·27
	O_2	16·00	72·73
	CO_2	22·00	100·00
Silicic acid	Si	14·00	46·67
	O_2	16·00	53·33
	SiO_2	30·00	100·00
Nitric acid	N	14·04	25·98
	O_5	40·00	74·02
	NO_5	54·04	100·00
Chloric acid	Cl	35·46	46·99
	O_5	40·00	53·01
	ClO_5	75·46	100·00

TABLE VI.

REDUCTION OF COMPOUNDS FOUND, TO CONSTITUENTS SOUGHT, BY SIMPLE MULTIPLICATION OR DIVISION.

This Table contains only some of the more frequently occurring compounds; the formulæ preceded by ! give absolutely accurate results. None of the equivalent weights used in the Table have been appreciably changed in consequence of recalculation or of new determinations. The effect produced by adopting MARIGNAC's equivalent weight (Mg = 12·185) for the calculation of magnesia, and of phosphoric acid, from the weight of the pyrophosphate of magnesia, is given in the footnotes.

FOR INORGANIC ANALYSIS.

CARBONIC ACID.

! Carbonate of lime × 0·44 = Carbonic acid.

CHLORINE.

Chloride of silver × 0·2473 = Chlorine.

COPPER.

Oxide of copper × 0·79849 = Copper.

IRON.

! Ferric oxide × 0·7 = 2 iron.

! Ferric oxide × 0·9 = 2 Ferrous oxide.

LEAD.

Oxide of lead × 0·92825 = Lead.

MAGNESIA.

Pyrophosphate of magnesia × 0·36036 = 2 Magnesia.*

MANGANESE.

Manganosomanganic oxide × 0·72052 = 3 Manganese.

Manganosomanganic oxide × 0·93013 = 3 Manganous oxide.

PHOSPHORIC ACID.

Pyrophosphate of magnesia × 0·63964 = Phosphoric acid.†

POTASSA.

Chloride of Potassium × 0·5246 = Potassium.

Sulphate of potassa × 0·54092 = Potassa.

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* If MARIGNAC'S most recent equivalent of magnesium (Mg = 12·185) be taken, this will be pyrophosphate of magnesia × 0·36249 = 2 magnesia.

† Taking Mg = 12·185 (MARIGNAC), pyrophosphate of magnesia × 0·63751 = Phosphoric acid.

Potassium platinochloride × 0·3056 * = Chloride of potassium.

Potassium platinochloride × 0·19308 = Potassa.

SODA.

Chloride of sodium × 0·5306 = Soda.

Sulphate of soda × 0·43694 = Soda.

SULPHUR.

Sulphate of baryta × 0·13734 = Sulphur.

SULPHURIC ACID.

Sulphate of baryta × 0·34335 = Sulphuric acid.

ELEMENTARY ANALYSIS OF ORGANIC SUBSTANCES.

CARBON.

$$\left.\begin{array}{c} \text{Carbonic acid} \times 0{\cdot}2727 \\ \text{or} \\ \dfrac{\text{Carbonic acid}}{3{\cdot}6667} \\ \text{or} \\ \dfrac{\text{Carbonic acid} \times 3}{11} \end{array}\right\} = \text{Carbon.}$$

HYDROGEN.

$$\left.\begin{array}{c} \text{Water} \times 0{\cdot}1111 \\ \text{or} \\ \dfrac{\text{Water}}{9} \end{array}\right\} = \text{Hydrogen.}$$

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* See this vol. p. 552.

TABLE

This gives the Amount of the Constituent sought for every unit
adopted in this book. Those compounds, the numbers for which are
the corresponding elements (see Tables II. and IV.), are indicated by
p. 97, but for "Table IV." (line 4, p. 97) read "Table VII."

Elements.	Found.	Sought.	1
Aluminium $Al=13{\cdot}75$	Alumina* $Al_2O_3=51{\cdot}50$	Aluminium $Al_2=27{\cdot}50$	0·53398
(Ammonium) $NH_4=18{\cdot}04$	Chloride of Ammonium $NH_4Cl=53{\cdot}50$	Ammonia $NH_3=17{\cdot}04$	0·31851
	Platinochloride of ammonium* $NH_4Cl, PtCl_2=223{\cdot}01$	Oxide of ammonium $NH_4O=26{\cdot}04$	0·11677
	Platinochloride of ammonium* $NH_4Cl,PtCl_2=223{\cdot}01$	Ammonia $NH_3=17{\cdot}04$	0·07641
Antimony $Sb=122$	Teroxide of antimony* $SbO_3=146$	Antimony $Sb=122$	0·83562
	Tersulphide of antimony* $SbS_3=170$	Antimony $Sb=122$	0·71765
	Tersulphide of antimony* $SbS_3=170$	Teroxide of antimony $SbO_3=146$	0·85882
	Pentasulphide of antimony* $SbS_5=202$	Antimony $Sb=122$	0·60396
	Pentasulphide of antimony* $SbS_5=202$	Teroxide of antimony $SbO_3=146$	0·72277
	Antimonate of oxide of antimony* $SbO_4=154$	Antimony $Sb=122$	0·79221
	Antimonate of oxide of antimony* $SbO_4=154$	Teroxide of antimony $SbO_3=146$	0·94805
Arsenic $As=75$	Arsenious acid $AsO_3=99$	Arsenic $As=75$	0·75758
	Arsenic acid $AsO_5=115$	Arsenic $As=75$	0·65217
	Arsenic acid $AsO_5=115$	Arsenious acid $AsO_3=99$	0·86087
	Tersulphide of arsenic $AsS_3=123$	Arsenic $As=75$	0·60976
	Tersulphide of arsenic $AsS_3=123$	Arsenious acid $AsO_3=99$	0·80488
	Pentasulphide of arsenic $AsS_5=155$	Arsenic $As=75$	0·48387
	Pentasulphide of arsenic $AsS_5=155$	Arsenious acid $AsO_3=99$	0·63871
	Arsenate of ammonia and magnesia* $2MgO,NH_4O,AsO_5,HO=190{\cdot}04$	Arsenic $As=75$	0·39465

VII.

of weight of the compound found, based upon the equivalent weights appreciably affected by the recalculation or by new determinations of an asterisk (*). For the method of using the Tables, see this vol.

2	3	4	5	6	7	8	9
1·06796	1·60194	2·13592	2·66990	3·20389	3·73787	4·27185	4·80583
0·63701	0·95551	1·27402	1·59252	1·91103	2·22985	2·54804	2·86654
0·23353	0·35030	0·46706	0·58383	0·70060	0·81736	0·93413	1·05089
0·15282	0·22923	0·30564	0·38205	0·45845	0·53486	0·61127	0·68768
1·67123	2·50685	3·34247	4·17808	5·01370	5·84931	6·68493	7·52055
1·43529	2·15294	2·87059	3·58824	4·30588	5·02353	5·74118	6·45882
1·71765	2·57647	3·43530	4·29412	5·15294	6·01177	6·87059	7·72942
1·20792	1·81188	2·41584	3·01980	3·62376	4·22772	4·83168	5·43564
1·44554	2·16832	2·89109	3·61386	4·33663	5·05940	5·78218	6·50495
1·58442	2·37662	3·16883	3·96104	4·75325	5·54546	6·33766	7·12987
1·89610	2·84416	3·79221	4·74026	5·68831	6·63636	7·58442	8·53247
1·51515	2·27273	3·03030	3·78788	4·54545	5·30303	6·06061	6·81818
1·30435	1·95652	2·60870	3·26087	3·91304	4·56522	5·21739	5·86957
1·72174	2·58261	3·44348	4·30435	5·16522	6·02609	6·88696	7·74783
1·21951	1·82927	2·43902	3·04878	3·65854	4·26829	4·87805	5·48780
1·60976	2·41463	3·21951	4·02439	4·82927	5·63415	6·43902	7·24390
0·96774	1·45161	1·93548	2·41935	2·90323	3·38710	3·87097	4·35484
1·27742	1·91613	2·55484	3·19355	3·83226	4·47097	5·10968	5·74839
0·78931	1·18396	1·57862	1·97327	2·36792	2·76258	3·15723	3·55189

TABLE

Elements.	Found.	Sought.	1
	Arsenate of ammonia and magnesia* $2MgO,NH_4O,AsO_5,HO=190{\cdot}04$	Arsenious acid $AsO_3=99$	0·52094
	Arsenate of magnesia* $2MgO,AsO_5=155$	Arsenic $As=75$	0·48387
	Arsenate of magnesia* $2MgO,AsO_5=155$	Arsenious acid $AsO_3=99$	0·63871
Barium $Ba=68{\cdot}50$	Baryta $BaO=76{\cdot}50$	Barium $Ba=68{\cdot}50$	0·89543
	Sulphate of baryta $BaO,SO_3=116{\cdot}50$	Baryta $BaO=76{\cdot}50$	0·65665
	Carbonate of baryta $BaO,CO_2=98{\cdot}50$	Baryta $BaO=76{\cdot}50$	0·77665
	Silicofluoride of barium $BaFl,SiFl_2=139{\cdot}5$	Baryta $BaO=76{\cdot}50$	0·54839
Bismuth $Bi=208{\cdot}00$	Teroxide of bismuth $BiO_3=232{\cdot}00$	Bismuth $Bi=208{\cdot}00$	0·89655
	Sulphide of bismuth $BiS_3=256{\cdot}00$	Bismuth $Bi=208{\cdot}00$	0·81250
Boron $B=11{\cdot}00$	Boric acid $BO_3=35$	Boron $B=11{\cdot}00$	0·31429
	Borofluoride of potassium $KF,BF_3=126{\cdot}13$	Boron $B=11{\cdot}00$	0·08721
Bromine $Br=79{\cdot}95$	Bromine of silver $AgBr=187{\cdot}88$	Bromine $Br=79{\cdot}95$	0·42554
Cadmium $Cd=56{\cdot}00$	Oxide of calcium $CdO=64{\cdot}00$	Cadmium $Cd=56$	0·87500
	Sulphate of cadmium $CdO,SO_3=104{\cdot}00$	Cadmium $Cd=56$	0·53846
	Sulphate of cadmium $CdO,SO_3=104{\cdot}00$	Oxide of cadmium $CdO=64{\cdot}00$	0·61539
	Sulphide of cadmium $CdS=72{\cdot}00$	Cadmium $Cd=56$	0·77778
	Sulphide of cadmium $CdS=72{\cdot}00$	Oxide of cadmium $CdO=64{\cdot}00$	0·88889
Calcium $Ca=20$	Lime $CaO=28$	Calcium $Ca=20$	0·71429
	Sulphate of lime $CaO,SO_3=68$	Lime $CaO=28$	0·41176
	Carbonate of lime $CaO,CO_2=50$	Lime $CaO=28$	0·56000
Carbon $C=6$	Carbonic acid $CO_2=22$	Carbon $C=6$	0·27273
Chlorine $Cl=35{\cdot}46$	Chloride of silver $AgCl=143{\cdot}39$	Chlorine $Cl=35{\cdot}46$	0·24730
	Silver $Ag=107{\cdot}93$	Chlorine $Cl=35{\cdot}46$	0·32855
Chromium $Cr=26{\cdot}24$	Sesquioxide of Chromium* $Cr_2O_3=76{\cdot}48$	Chromium $Cr_2=52{\cdot}48$	0·68619

VII.—(*continued.*)

2	3	4	5	6	7	8	9
1·04189	1·56283	2·08377	2·60472	3·12566	3·64660	4·16754	4·68849
0 96774	1·45161	1·93548	2·41936	2·90323	3·38710	3·87097	4·35484
1 27742	1·91613	2·55484	3·19355	3·83226	4·47097	5·10968	5·74839
1·79085	2 68628	3·58170	4·47713	5·37255	6·26798	7·16340	8·05883
1·31330	1·96996	2·62661	3·28326	3·93991	4·59656	5·25322	5·90987
1·55330	2·32995	3·10660	3·88325	4·65990	5·43655	6·21320	6·98985
1 09677	1·64516	2·19355	2·74194	3·29032	3·83871	4·38710	4·93548
1·79310	2·68966	3·58621	4·48276	5·37931	6·27586	7·17242	8·06897
1·62500	2·43750	3·25000	4·06250	4·87500	5·68750	6·50000	7·31250
0·62857	0·94286	1·25714	1·57143	1 88572	2·20000	2·51429	2·82857
0·17442	0·26163	0·34885	0·43606	0·52327	0·61048	0·69769	0·78490
0·85108	1·27661	1·70215	2·12769	2·55323	2·97877	3·40430	3·82984
1·75000	2·62500	3·50000	4·37500	5·25000	6·12500	7·00000	7·87500
1·07692	1·61539	2·15385	2·69231	3·23077	3·76923	4·30770	4·84616
1·23077	1·84616	2·46154	3·07693	3·69231	4·30770	4·92308	5·53847
1·55556	2·33333	3·11111	3·88889	4·66667	5·44445	6·22222	7·00000
1·77778	2·66667	3·55556	4·44445	5·33333	6·22222	7·11111	8·00000
1·42857	2·14286	2·85714	3·57143	4·28571	5·00000	5·71429	6·42857
0·82353	1·23529	1·64706	2·05882	2·47059	2·88235	3·29412	3·70588
1·12000	1·68000	2·24000	2·80000	3 36000	3·92000	4·48000	5·04000
0·54545	0·81818	1·09091	1·36364	1·63636	1·90909	2·18182	2·45454
0·49460	0·74189	0·98919	1 23649	1·48379	1·73108	1·97838	2·22568
0·65709	0·98564	1 31418	1·64273	1·97128	2·29982	2·62837	2·95691
1·37238	2·05858	2·74477	3·43096	4·11715	4·80334	5·48954	6 17573

TABLE

Elements.	Found.	Sought.	1
	Sesquioxide of chromium * $Cr_2O_3=76{\cdot}48$	Chromic acid $2CrO_3=100{\cdot}48$	1.31381
	Chromate of lead * $PbO,CrO_3=161{\cdot}74$	Chromic acid $CrO_3=50{\cdot}24$	0·31062
	Chromate of baryta * $BaO,CrO_3=126{\cdot}74$	Chromic acid $CrO_3=50{\cdot}24$	0·39640
Cobalt $Co=29{\cdot}50$	Protoxide of cobalt $CoO=37{\cdot}50$	Cobalt $Co=29{\cdot}50$	0·78667
	Cobalt * $Co=29{\cdot}50$	Protoxide of cobalt $CoO=37{\cdot}50$	1·27119
	Sulphate of protoxide of cobalt * $CoO,SO_3=77{\cdot}50$	Protoxide of cobalt $CoO=37{\cdot}50$	0·48387
	Nitrite of sesquioxide of cobalt * and potassa $Co_2O_3,3KO,5NO_3+2HO=432{\cdot}59$	Protoxide of cobalt $2CoO=75{\cdot}00$	0·17337
	Nitrite of sesquioxide of cobalt * and potassa $Co_2,O_33KO,5NO_3+2HO=432{\cdot}59$	Cobalt $2Co=59{\cdot}00$	0·13639
Copper $Cu=31{\cdot}70$	Oxide of copper $CuO=39{\cdot}70$	Copper $Cu=31{\cdot}70$	0·79849
	Cuprous sulphide $Cu_2S=79{\cdot}40$	Copper $2Cu=63{\cdot}40$	0·79849
Fluorine $Fl=19{\cdot}00$	Fluoride of calcium $CaF=39{\cdot}00$	Fluorine $F=19{\cdot}00$	0·48718
	Fluoride of silicon $SiF_2=52$	Fluorine $2F=38{\cdot}00$	0·73077
Hydrogen $H=1$	Water $HO=9{\cdot}00$	Hydrogen $H=1{\cdot}00$	0·11111
Iodine $I=126{\cdot}85$	Iodide of silver $AgI=234{\cdot}78$	Iodine $I=126{\cdot}85$	0·54029
	Iodide of palladium * $PdI=180{\cdot}14$	Iodine $I=126{\cdot}85$	0·70417
Iron $Fe=28{\cdot}00$	Ferric oxide $Fe_2O_3=80$	Iron $Fe_2=56$	0·70000
	Ferric oxide $Fe_2O_3=80$	Ferrous oxide $2FeO=72$	0·90000
	Sulphide of iron $FeS=44$	Iron $Fe=28{\cdot}00$	0·63636
Lead $Pb=103{\cdot}50$	Oxide of lead $PbO=111{\cdot}50$	Lead $Pb=103{\cdot}50$	0·92825
	Sulphate of lead $PbO,SO_3=151{\cdot}50$	Lead $Pb=103{\cdot}50$	0·68317
	Sulphate of lead $PbO,SO_3=151{\cdot}50$	Oxide of lead $PbO=111{\cdot}50$	0·73597
	Chloride of lead $PbCl=138{\cdot}96$	Lead $Pb=103{\cdot}50$	0·74482
	Chloride of lead $PbCl=138{\cdot}96$	Oxide of lead $PbO=111{\cdot}50$	0·80239

VII.—(*continued.*)

2	3	4	5	6	7	8	9
2·62762	3·94142	5·25523	6·56904	7·88285	9·19666	10·51046	11·82427
0·62124	0·93187	1·24249	1·55311	1·86373	2·17435	2·48498	2·79560
0·79280	1·18921	1·58561	1·98201	2·37841	2·77481	3·17122	3·56762
1·57333	2·36000	3·14667	3·93334	4·72000	5·55067	6·29334	7·08000
2·54237	3·81356	5·08475	6·35593	7·62712	8·89831	10·16949	11·44067
0·96774	1·45161	1·93548	2·41936	2·90323	3·38710	3·87097	4·35484
0·34675	0·52012	0·69350	0·86687	1·04024	1·21362	1·38699	1·56037
0·27278	0·40916	0·54555	0·68194	0·81833	9·95472	1·09110	1·22749
1·59698	2·39547	3·19395	3·99244	4·79093	5·58942	6·38791	7·18640
1·59698	2·39547	3·19395	3·99244	4·79093	5·58942	6·38791	7·18640
0·97436	1·46154	1·94872	2·43590	2·92307	3·41027	3·89743	4·38461
1·46154	2·19231	2.92308	3·65385	4·38461	5·11538	5·84615	6·57692
0·22222	0·33333	0·44444	0·55556	0·66667	0·77778	0·88889	1·00000
1·08059	1·62088	2·16117	2·70147	3·24176	3·78205	4·32234	4·86264
1·40835	2·11252	2·81670	3·52087	4·22504	4·92922	5·63339	6·33757
1·40000	2·10000	2·80000	3·50000	4·20000	4·90000	5·60000	6·30000
1·80000	2·70000	3·60000	4·50000	5·40000	6·30000	7·20000	8·10000
1·27273	1·90909	2·54546	3·18182	3·81818	4·45455	5·09091	5·72728
1·85650	2·78475	3·71300	4·64126	5·56951	6·49776	7·42601	8·35426
1·36634	2·04951	2·73267	3·41584	4·09901	4·78218	5·46534	6·14851
1·47195	2·20792	2·94390	3·67987	4·41584	5·15182	5·88779	6·62377
1·48964	2·23446	2·97928	3·72409	4·46891	5·21373	5·95855	6·70337
1·60478	2·40717	3·20956	4·01195	4·81433	5·61672	6·41911	7·22150

TABLE

Elements.	Found.	Sought.	1
	Sulphide of lead PbS = 119·50	Lead Pb = 103·50	0·86611
	Sulphide of lead PbS = 119·50	Oxide of lead PbO = 111·50	0·93305
Lithium Li = 7·02	Lithia LiO = 15·02	Lithium Li = 7·02	0·46738
	Sulphate of lithia LiO,SO_3 = 55·02	Lithia LiO = 15·02	0·27299
	Basic phosphate of lithia $3LiO,PO_5$ = 116·06	Lithia 3LiO = 45·06	0·38825
Magnesium Mg = 12·00	Magnesia* MgO = 20	Magnesium Mg = 12·00	0·60000
	Sulphate of magnesia* MgO,SO_3 = 60	Magnesia MgO = 20·00	0·33333
	Pyrophosphate of magnesia* $2MgO,PO_5$ = 111	Magnesia 2MgO = 40·00	0·36036
Manganese Mn = 27·5	Manganous oxide MnO = 35·5	Manganese Mn = 27·5	0·77465
	Sesquioxide of manganese Mn_2O_3 = 79·00	Manganese 2Mn = 55·00	0·69620
	Manganosomanganic oxide Mn_3O_4 = 114·50	Manganese 3Mn = 82·50	0·72052
	Sulphide of manganese MnS = 43·5	Manganese Mn = 27·5	0·63218
	Sulphide of manganese MnS = 43·5	Protoxide of manganese MnO = 35·5	0·81609
	Sulphate of manganous oxide MnO,SO_3 = 75·5	Protoxide of manganese MnO = 35·5	0·47020
Mercury Hg = 100·00	Mercuric oxide HgO = 108·00	Mercury Hg = 100·00	0·92593
	Mercury Hg_2 = 200	Mercurous oxide Hg_2O = 208·00	1·04000
	Mercury Hg = 100	Mercuric oxide HgO = 108·00	1·08000
	Mercurous chloride Hg_2Cl = 235·46	Mercury 2Hg = 200	0·84940
	Mercuric sulphide HgS = 116·00	Mercury Hg = 100	0·86207
Nickel Ni = 29·5	Protoxide of nickel* NiO = 37·5	Nickel Ni = 29·50	0·18667
	Nickel Ni = 29·50	Protoxide of nickel NiO = 37·5	0·27119
Nitrogen N = 14·04	Platinochloride of ammonium* $NH_4Cl,PtCl_2$ = 223·01	Nitrogen N = 14·04	0·06296
	Platinum* Pt = 98·59	Nitrogen N = 14·04	0·14241

VII.—(*continued.*)

2	3	4	5	6	7	8	9
1·73222	2·59833	3·46444	4·33055	5·19665	6·06276	6·92887	7·79498
1·86611	2·79916	3·73222	4·66527	5·59832	6·53138	7·46443	8·39749
0.93475	1·40213	1·86951	2·33688	2·80426	3·27164	3·73902	4·20639
0·54598	0·81898	1·09197	1·36496	1·63795	1·91094	2·18394	2·45693
0·77649	1·16474	1·55299	1·94124	2·32948	2·71773	3·10598	3·49423
1·20000	1·80000	2·40000	3·00000	3·60000	4·20000	4·80000	5·40000
0·66667	1 00000	1·33333	1·66667	2·00000	2·33333	2·66667	3 00000
0·72072	1·08108	1·44144	1·80180	2·16216	2·52252	2·88288	3·24324
1·54930	2·32394	3·09859	3·87324	4 64789	5·42254	6·19718	6·97183
1·39241	2·08861	2·78481	3·48102	4·17722	4·87342	5·56962	6 26583
1·44105	2·16157	2·88210	3·60262	4·32314	5·04367	5·76419	6·48472
1·26437	1·89655	2·52874	3·16092	3·79310	4·42529	5·05747	5·68966
1·63218	2·44828	3·26437	4·08046	4·89655	5 71264	6·52874	7·34483
0·94040	1·41060	1·88080	2·35100	2·82119	3·29139	3·76159	4·23179
1·85185	2·77778	3·70370	4·62963	5·55556	6·48148	7·40741	8·33333
2·08000	3·12000	4·16000	5·20000	6·24000	7·28000	8·32000	9·36000
2·16000	3·24000	4·32000	5·40000	6·48000	7·56000	8·64000	9·72000
1·69880	2·54820	3·39760	4·24701	5·09641	5·94581	6 79521	7·64461
1·72414	2·58621	3·44828	4·31035	5·17241	6·03448	6·89655	7·75862
1·57333	2·36000	3·14667	3·93334	4·72000	5 50667	6·29334	7·08000
2·54237	3·81356	5·08475	6·35593	7·62712	8·89831	10·16949	11·44067
0·12591	0·18887	0·25183	0·31479	0·37774	0·44070	0·50366	0·56661
0·28482	0·42722	0·56963	0·71204	0·85445	0·99686	1·13926	1·28167

TABLE

Elements.	Found.	Sought.	1
	Cyanide of silver $AgC_2N=133·97$	Hydrocyanic acid $HC_2N=27·04$	0·20184
	Cyanide of silver $AgC_2N=133·97$	Cyanogen $C_2N=26·04$	0·19437
Oxygen $O=8·00$	Alumina * $Al_2O_3=51·50$	Oxygen $3O=24$	0·46602
	Teroxide of antimony * $SbO_3=146$	Oxygen $3O=24$	0·16438
	Arsenious acid $AsO_3=99·00$	Oxygen $3O=24$	0·24242
	Arsenic acid $AsO_5=115·00$	Oxygen $5O=40$	0·34783
	Baryta $BaO=76·50$	Oxygen $O=8$	0·10457
	Teroxide of bismuth $BiO_3=232·00$	Oxygen $3O=24$	0·10345
	Oxide of cadmium $CdO=64·00$	Oxygen $O=8$	0·12500
	Sesquioxide of chromium * $Cr_2O_3=76·48$	Oxygen $3O=24$	0·31381
	Protoxide of cobalt * $CoO=37·50$	Oxygen $O=8$	0·21333
	Oxide of copper $CuO=39·70$	Oxygen $O=8$	0·20151
	Ferric oxide $Fe_2O_3=80·00$	Oxygen $3O=24$	0·30000
	Ferrous oxide $FeO=36·00$	Oxygen $O=8$	0·22222
	Oxide of lead $PbO=111·50$	Oxygen $O=8$	0·07175
	Lime (oxide of calcium) $CaO=28·00$	Oxygen $O=8$	0·28571
	Magnesia * $MgO=20·00$	Oxygen $O=8$	0·40000
	Manganous oxide $MnO=35·50$	Oxygen $O=8$	0·22535
	Manganosomanganic oxide $Mn_3O_4=114·50$	Oxygen $4O=32$	0·27948
	Sesquioxide of manganese $Mn_2O_3=79·00$	Oxygen $3O=24$	0·30380
	Mercuric oxide $HgO=108·00$	Oxygen $O=8$	0·07407
	Mercurous oxide $Hg_2O=208·00$	Oxygen $O=8$	0·03846
	Protoxide of nickel * $NiO=37·50$	Oxygen $O=8$	0·21333
	Potassa $KO=47·13$	Oxygen $O=8$	0·16974

VII.—(*continued.*)

2	3	4	5	6	7	8	9
0·40367	0·60551	0·80735	1·00918	1·21102	1·41285	1·61469	1·81653
0·38874	0·58312	0·77749	0·97186	1·16623	1·36060	1·55498	1·74935
0·93204	1·39806	1·86408	2·33010	2·79611	3·26213	3·72815	4·19417
0·32877	0·49315	0·65754	0·82192	0·98630	1·15069	1·31507	1·47946
0·48485	0·72727	0·97070	1·21212	1·45458	1·69697	1·93939	2·18182
0·69565	1·04348	1·39130	1·73913	2·08696	2·43478	2·78261	3·13043
0·20915	0·31372	0·41830	0·52287	0·62745	0·73202	0·83660	0·94117
0·20690	0·31034	0·41379	0·51724	0·62069	0·72414	0·82758	0·93103
0·25000	0·37500	0·50000	0·62500	0·75000	0·87500	1·00000	1·12500
0·62761	0·94142	1·25523	1·56903	1·88284	2·19665	2·51046	2·82426
0·42667	0·64000	0·85333	1·06666	1·28000	1·49333	1·70666	1·92000
0·40302	0·60453	0·80604	1·00756	1·20907	1·41058	1·61209	1·81360
0·60000	0·90000	1·20000	1·50000	1·80000	2·10000	2·40000	2·70000
0·44444	0·66667	0·88889	1·11111	1·33333	1·55556	1·77778	2·00000
0·14350	0·21525	0·28700	0·35874	0·43049	0·50224	0·57399	0·64574
0·57143	0·85714	1·14286	1·42857	1·71429	2·00000	2·28571	2·57143
0·80000	1·20000	1·60000	2·00000	2·40000	2·80000	3·20000	3·60000
0·45070	0·67606	0·90141	1·12676	1·35211	1·57746	1·80282	2·02817
0·55895	0·83843	1·11790	1·39738	1·67686	1·95633	2·23581	2·51528
0·60759	0·91139	1·21519	1·51898	1·82278	2·12658	2·43038	2·73417
0·14815	0·22222	0·29630	0·37037	0·44444	0·51852	0·59259	0·66667
0·07692	0·11538	0·15385	0·19231	0·23077	0·26923	0·30769	0·34615
0·42667	0·64000	0·85333	1·06666	1·28000	1·49333	1·70666	1·92000
0·33949	0·50923	0·67897	0·84871	1·01846	1·18820	1·35794	1·52769

TABLE

Elements.	Found.	Sought.	1
Oxygen $\mathrm{O}=8\cdot00$	Silicic acid $\mathrm{SiO_2}=30\cdot00$	Oxygen $2\mathrm{O}=16$	0·53333
	Oxide of silver $\mathrm{AgO}=115\cdot93$	Oxygen $\mathrm{O}=8$	0·06901
	Soda $\mathrm{NaO}=31\cdot04$	Oxygen $\mathrm{O}=8$	0·25773
	Strontia $\mathrm{SrO}=51\cdot75$	Oxygen $\mathrm{O}=8$	0·15459
	Stannic acid $\mathrm{SnO_2}=75\cdot00$	Oxygen $2\mathrm{O}=16$	0·21333
	Water $\mathrm{HO}=9\cdot00$	Oxygen $\mathrm{O}=8$	0·88889
	Oxide of zinc $\mathrm{ZnO}=40\cdot53$	Oxygen $\mathrm{O}=8$	0·19738
Phosphorus $\mathrm{P}=31\cdot00$	Phosphoric acid $\mathrm{PO_5}=71\cdot00$	Phosphorus $\mathrm{P}=31\cdot00$	0·43662
	Pyrophosphate of magnesia * $2\mathrm{MgO,PO_5}=111$	Phosphorus $\mathrm{P}=31\cdot00$	0·27928
	Pyrophosphate of magnesia * $2\mathrm{MgO,PO_5}=111$	Phosphoric acid $\mathrm{PO_5}=71\cdot00$	0·63964
	Ferric phosphate $\mathrm{Fe_2O_3,PO_5}=151\cdot00$	Phosphoric acid $\mathrm{PO_5}=71\cdot00$	0·47020
	Phosphate of silver $3\mathrm{AgO,PO_5}=418\cdot79$	Phosphoric acid $\mathrm{PO_5}=71\cdot00$	0·16954
	Phosphate of sesquioxide of uranium $2\mathrm{Ur_2O_3,PO_5}=356\cdot00$	Phosphoric acid $\mathrm{PO_5}=71\cdot00$	0·19910
Potassium $\mathrm{K}=39\cdot13$	Potassa $\mathrm{KO}=47\cdot13$	Potassium $\mathrm{K}=39\cdot13$	0·83026
	Sulphate of potassa $\mathrm{KO,SO_3}=87\cdot13$	Potassa $\mathrm{KO}=47\cdot13$	0·54092
	Nitrate of potassa $\mathrm{KO,NO_5}=101\cdot17$	Potassa $\mathrm{KO}=47\cdot13$	0·46585
	Chloride of potassium $\mathrm{KCl}=74\cdot59$	Potassium $\mathrm{K}=39\cdot13$	0·52460
	Chloride of potassium $\mathrm{KCl}=74\cdot59$	Potassa $\mathrm{KO}=47\cdot13$	0·63185
	Platinochloride of potassium † $\mathrm{KCl,PtCl_2}=244\cdot10$	Potassa $\mathrm{KO}=47\cdot13$	0·19308
	Platinochloride of potassium † $\mathrm{KCl,PtCl_2}=244\cdot10$	Chloride of potassium $\mathrm{DCl}=74\cdot59$	0·30557
Silicon $\mathrm{Si}=14\cdot00$	Silicic acid $\mathrm{SiO_2}=30\cdot00$	Silicon $\mathrm{Si}=14\cdot00$	0·46667
Silver $\mathrm{Ag}=107\cdot93$	Oxide of silver $\mathrm{AgO}=115\cdot93$	Silver $\mathrm{Ag}=107\cdot93$	0 93099
	Chloride of silver $\mathrm{AgCl}=143\cdot39$	Silver $\mathrm{Ag}=107\cdot93$	0·75270
	Chloride of silver $\mathrm{AgCl}=143\cdot39$	Oxide of silver $\mathrm{Ag}=115\cdot93$	0·80849

† See this vol. p. 552.

VII.—(*continued.*)

2	3	4	5	6	7	8	9
1·06667	1·60000	2·13333	2·66667	3·20000	3·73333	4·26667	4·80000
0·13801	0·20702	0·27603	0·34503	0·41404	0·48305	0·55206	0·62106
0·51546	0·77320	1·03093	1·28866	1·54639	1·80412	2·06186	2.31959
0·30918	0·46377	0.61836	0·77294	0·92753	1·08212	1·23671	1·39130
0·42667	0·64000	0·85333	1·06667	1·28000	1·49333	1·70667	1·92000
1·77778	2·66667	3·55556	4·44445	5·33333	6·22222	7·11111	8·00000
0·39477	0·59215	0·78954	0·98692	1·18431	1·38169	1·57908	1·77646
0·87324	1·30986	1·74648	2·18310	2·61972	3·05634	3·49296	3·92958
0·55856	0·83784	1·11712	1·39640	1·67567	1·95495	2·23423	2·51351
1·27928	1·91892	2·55856	3·19820	3·83784	4·47748	5·11712	5·75676
0·94040	1·41060	1·88080	2·35100	2·82119	3·29139	3·76159	4·23179
0·33907	0·50861	0·67814	0·84768	1·01722	1·18675	1·35629	1·52582
0·39821	0·59731	0·79641	0·99551	1·19462	1·39372	1·59282	1·79193
1·66051	2·49077	3·32103	4·15129	4·98154	5·81180	6·64206	7·47231
1·08183	1·62275	2·16366	2·70458	3·24550	3·78641	4·32733	4·86824
0·93170	1·39755	1·86340	2·32925	2·79510	3·26095	3·72680	4·19265
1·04920	1·57380	2·09840	2·62301	3·14761	3·67221	4·19681	4·72141
1·26371	1·89556	2·52742	3·15927	3·79112	4·42298	5·05483	5·68669
0·38615	0·57923	0·77231	0·96538	1·15846	1·35154	1·54461	1·73769
0·61114	0·91671	1·22229	1·52786	1·83343	2·13900	2·44457	2·75014
0·93333	1·40000	1·86667	2·33333	2·80000	3·26667	3·73333	4·20000
1·86199	2·79298	3·72397	4·65497	5·58596	6·51695	7·44794	8·37894
1·50540	2·25811	3·01081	3·76351	4·51621	5·26892	6·02162	6·77432
1·61699	2·42548	3·23398	4·04247	4·85096	5·65946	6·46795	7·27645

TABLE

Elements.	Found.	Sought.	1
Sodium Na = 23·04	Soda NaO = 31·04	Sodium Na = 23·04	0·74227
	Sulphate of soda NaO,SO_3 = 71·04	Soda NaO = 31·04	0·43694
	Nitrate of soda NaO,NO_5 = 85·08	Soda NaO = 31·04	0·36483
	Carbonate of soda NaO,CO_2 = 53·04	Soda NaO = 31·04	0·58522
	Chloride of sodium $NaCl$ = 58·50	Soda NaO = 31·04	0·53060
	Chloride of sodium $NaCl$ = 58·50	Sodium Na = 23·04	0·39385
Strontium Sr = 43·75	Strontia SrO = 51·75	Strontium Sr = 43·75	0·84541
	Sulphate of strontia SrO,SO_3 = 91·75	Strontia SrO_2 = 51·75	0·56403
	Carbonate of strontia SrO,Co_2 = 73·75	Strontia SrO = 51·75	0·70170
Sulphur S = 16·00	Sulphate of baryta BaO,SO_3 = 116·50	Sulphuric acid SO_3 = 40·00	0·34335
	Sulphate of baryta BaO,SO_3 = 116·50	Sulphur S = 16·00	0·13734
	Tersulphide of arsenic AsS_3 = 123	Sulphur $3S$ = 48·00	0·39024
Tin Sn = 59·00	Stannic oxide SnO_2 = 75·00	Tin Sn = 59·00	0·78667
	Stannic oxide SnO_2 = 75·00	Stannous oxide SnO = 67·00	0·89333
Zinc Zn = 32·53	Oxide of zinc ZnO = 40·53	Zinc Zn = 32·53	0·80262
	Sulphide of zinc ZnS = 48·53	Zinc Zn = 32·53	0·67031
	Sulphide of zinc ZnS = 48·53	Oxide of zinc ZnO = 40·53	0·83515

VII.— *(continued.)*

2	3	4	5	6	7	8	9
1·48454	2·22680	2·96907	3·71134	4·45361	5·19588	5·93814	6·68041
0·87387	1·31081	1·74775	2·18469	2·62162	3·05856	3·49550	3·93243
0·72967	1·09450	1·45933	1·82417	2·18900	2·55383	2·91866	3·28350
1·17044	1·75566	2·34088	2·92610	3·51131	4·09653	4·68175	5·26697
1.06120	1·59180	2·12239	2·65299	3·18359	3·71419	4·24478	4·77538
0·78769	1·18144	1·57538	1·96923	2·36308	2·75692	3·15077	3·54461
1·69082	2·53623	3·38164	4·22706	5·07247	5·91788	6·76329	7·60870
1·12807	1·69210	2·25613	2·82017	3·38420	3·94823	4·51226	5·07630
1·40339	2·10509	2·80678	3·50848	4·21017	4·91187	5·61356	6·31526
0·68670	1·03004	1·37339	1·71674	2·06009	2·40343	2·74678	3·09013
0·27468	0·41202	0·54936	0·68670	0·82403	0·96137	1·09871	1·23605
0·78049	1·17073	1·56098	1·95122	2·34146	2·73171	3·12195	3·51220
1·57333	2·36000	3·14667	3·93333	4·72000	5·50667	6·29333	7·08000
1·78667	2·68000	3·57333	4·46667	5·36000	6·25333	7·14667	8·04000
1·60523	2·40785	3·21046	4·01308	4·81569	5·61831	6·42092	7·22354
1·34061	2·01092	2·68123	3·35154	4·02184	4·69215	5·36246	6·03276
1·67031	2 50546	3·34062	4·17577	5·01092	5·84608	6·68123	7·51639

TABLE VIII.

SPECIFIC AND ABSOLUTE WEIGHTS OF SOME GASES.

	Specific weight, air = 1.	Specific weight, air = 1.	1 litre (1000 c.c.) of gas at 0° and 760 mm. pressure weights, in grams.
Atmospheric air	1·00000	1·00000	1·293635 *
Oxygen	1·10563 (RÉGNAULT)	1·10563	1·430282
	Calculated †	Determined ‡	
Hydrogen	0·06910	0·06927	0·089610
Water vapour	0·62191		
Carbon vapour	0·82922		
Carbonic acid	1·52024	1·52908	1·978071
Carbonic oxide	0·96742		
Marsh gas (methane)	0·55281		
Ethylene	0·96742		
Phosphorus vapour	4·28432		
Sulphur vapour	2·21126 §		
Sulphuretted hydrogen	1·17473		
Iodine vapour	8·76557		
Bromine vapour	5·52470		
Chlorine	2·45035		
Nitrogen	0·97019	0·97136	1·256585
Nitric oxide	1·03791		
Ammonia	0·58875		
Cyanogen	1·79941		

* For Berlin, calculated by W. LASCH (Chem. pharm. Centralbl. 1852, p. 148).

† The specific weights here given are calculated from the equivalents used in the book and based on the specific weight of Oxygen = 1·10563 as determined by RÉGNAULT.

‡ The values for Hydrogen, carbonic acid and nitrogen as determined by RÉGNAULT are given for comparison with the calculated values. From these the weights of a litre of the different gases at Berlin are reckoned taking the weight of a litre of atmospheric air in Berlin as the standard.

§ Sulphur vapour has not this specific weight below 800° to 1000°; at 450° to 500° it is 6·6.

TABLE IX.

COMPARISON OF DEGREES OF THE MERCURIAL THERMOMETER WITH THOSE OF THE AIR- OR HYDROGEN-THERMOMETER.

(ACCORDING TO CRAFTS.)*

Degrees of the mercurial thermometer.	Degrees of the air-thermometer.
110	110·02
120	120·04
130	130·09
140	140·16
150	150·25
160	160·33
170	170·35
180	180·34
190	190·32
200	200·27
210	210·18
220	220·08
230	229·98
240	239·86
250	249·74
260	259·61
270	269·50
280	279·37
290	289·12
300	298·79
310	308·40
320	317·97
330	327·52

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* Comptes rendus, 95, 836 and 910; Zeitschr. f. anal. Chem. 23, 526.—The figures are the mean of experiments with 15 thermometers. They hold good for lead glass containing 18°/₀ of oxide of lead, as well as for German soda glass. CRAFTS found no important difference between the two kinds of glass; the differences between his values and those arrived at by RÉGNAULT and others are accounted for by him from the circumstances that the composition of the glass of which thermometers were formerly made was very different from that of the glass now employed for this purpose.

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